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16. Abstract (Limit: 200 words)

This study compares six nonbauxitic alumina processes with the objective of selecting the two most promising candidate processes for further study. The comparisons cover both technical and economic aspects of alumina process plants of a commercial size in the United States. The processes considered were hydrochloric acid-clay (evaporative and gas-induced crystallization), nitric acid-clay, sulfurous acid-clay, anorthosite-lime sinter, and alunite. Technical appraisals for each process complete with process descriptions, heat and material balances, flowsheets, and equipment lists have been prepared based on published information available through the Bureau of Mines miniplant program and other nonproprietary sources. Technical and economic comparisons are made from which conclusions can be drawn for selecting the two most promising processes.

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ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN

Task 1 Final Report: Comparison of Six Processes

SEPTEMBER 1977

NOTICE

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department's Bureau of Mines or of the U.S. Government.

Contract No. JO265048

FOREWORD

This report was prepared by Kaiser Engineers, Oakland, California, under USBM Contract J0265048. The contract was initiated under the Metallurgy program. It was administered under the technical direction of Reno Metallurgy Research Center with Gerald B. McSweeney acting as Technical Project Officer. Ronald J. Simonich was the contract administrator for the Bureau of Mines. This report is a summary of the work recently completed as a part of this contract during the period October, 1976 to September, 1977. This report was submitted by the authors in September, 1977. The report contains no patentable features.

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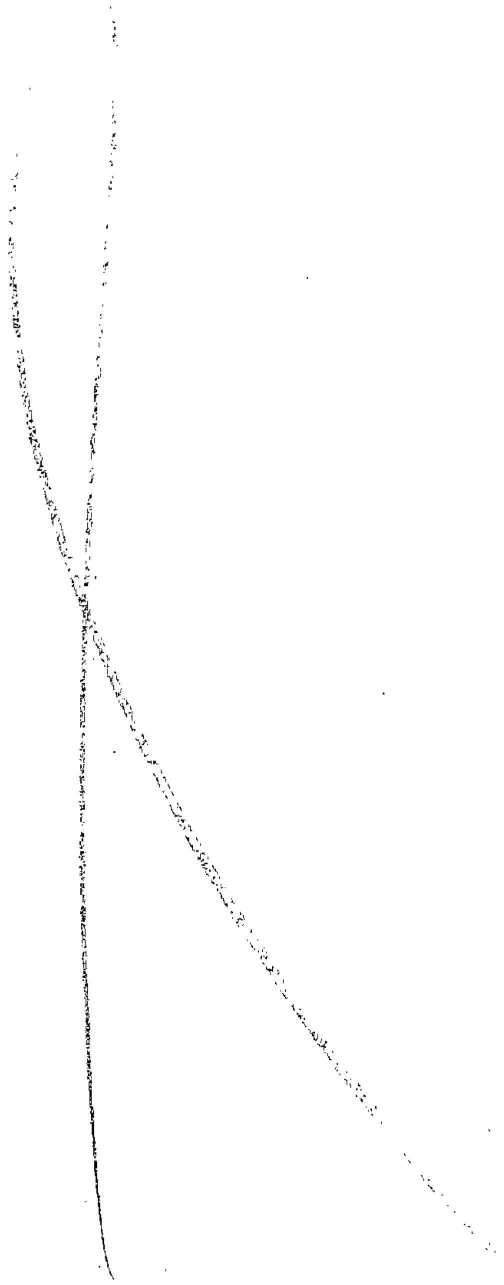

SUMMARY: PRINCIPAL CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to review the technical and economic merits of six alumina processes based on domestic nonbauxitic ores and choose the best two processes for further study.

The six processes reviewed were:

- Clay/Nitric Acid
- Clay/Hydrochloric Acid using Evaporative Crystallization
- Clay/Hydrochloric Acid using Gas-induced Crystallization
- Clay Sulfurous Acid
- Anorthosite/Lime-Sinter
- Alunite/Reduction Roast - Bayer Extraction

Based on capital and operating cost estimates, together with a technical analysis of each process, the study shows that the hydrochloric acid process using HCl gas-induced crystallization and the hydrochloric acid process using evaporative crystallization have the lowest cost and are therefore recommended for further study in Task 2.

1. INTRODUCTION

Practically all the aluminum produced in the U.S. today is based on mining bauxite, converting it to alumina, and refining the alumina to aluminum. Currently, the only domestic bauxite source for the U.S. alumina industry is in Arkansas. Worldwide deposits of bauxite indicate no international shortage, although in the first half of the 1970's, major bauxite-producing countries have raised the price of their bauxite exports 300 to 400% through taxes and levies. Thus, economic and other considerations raise some doubts as to the continued availability of adequate bauxite supplies to the U.S. at acceptable prices. This has spurred the search for domestic alternatives to bauxite.

This report is concerned with the producing of alumina from non-bauxitic domestic ore raw materials through six possible alternative processes. As an outgrowth of the long-term program of research on technologies for extracting alumina from domestic resources, the Bureau of Mines began on July 1, 1973, a mini-plant project to evaluate processes for recovering alumina from these resources. The purpose of the mini-plant project is to test and develop the most promising processes in a small scale pilot plant operation which would provide technical and economic data necessary for scaling up to commercial-size plants and for making rational decisions for selecting the alumina process technology that should be used in a 10- to 50-ton-per-day pilot plant. Subsequently in January 1974, companies having an interest in producing alumina were invited by the Bureau of Mines to join the mini-plant project on a cooperative, cost-sharing basis. Ten companies joined the program which is being conducted at the Boulder City Engineering Laboratory of the Bureau of Mines.

On September 30, 1976, the Bureau of Mines awarded Contract Number JO265048 entitled "Alumina Process Feasibility Study and preliminary Pilot Plant Design" to Kaiser Engineers in Oakland, California, with Kaiser Aluminum & Chemical Corporation as subcontractor. The work under this contract is divided into three distinct, separate, and consecutive tasks spanning a period of approximately 27 months.

This report covers the first of these tasks--Task 1. The objective of the task is to reduce the number of candidate processes from six to two. The six conceptual processes studied under this task are:

- Clay/Nitric Acid
- Clay/Hydrochloric Acid (Evaporative Crystallization)
- Clay/Hydrochloric Acid (HCl Gas Induced Crystallization)
- Clay/Sulfurous Acid
- Anorthosite/Lime - Sinter
- Alunite/Reduction Roast - Bayer Extraction

The basic technical and process data for the study was provided by the Bureau of Mines from data developed in the mini-plant program and also from past reports. In addition, technical and economic information was drawn from other published and unpublished sources and from the experience of Kaiser Engineers and its subcontractor, Kaiser Aluminum & Chemical Corporation. The references containing the information used in this report are listed in the Appendix.

2. TECHNICAL AND ECONOMIC COMPARISONS OF THE SIX PROCESSES

2.1 TECHNICAL COMPARISON OF THE SIX PROCESSES

Following is a summarized technical comparison of the six processes which are the subject of this report. Comparative costs presented elsewhere are a quantitative expression of part, but not all, of the information presented below.

2.1.1 Alumina from Clay via Nitric Acid Extraction

(1) This process employs nitric acid as the primary leaching reagent which is more costly and is expected to increase in cost relative to hydrochloric acid.

(2) The relative instability of the nitrate group results in some unavoidable nitrate losses as N_2 and N_2O.

(3) No fully satisfactory method of iron removal is known to be available. The use of ion exchange creates large streams containing HNO_3 and HCl. The use of substoichiometric HNO_3 leaching would require a considerable amount of additional equipment.

(4) The apparent poor separation factor in crystallization may require either a large crystallizer bleed stream or multiple $Al(NO_3)_3 \cdot 9H_2O$ crystallizations. Optimization of the crystallization section of the process would require extensive further study.

(5) This process requires that all H_2O in which $Al(NO_3)_3 \cdot 9H_2O$ is dissolved be evaporated in a step not necessary in the base case. The base case is defined in this report as the HCl/Clay-HCl gas induced crystallization process.

(6) The heat requirement for decomposition of $Al(NO_3)_3 \cdot 9H_2O$ is approximately 50% greater than for decomposition of $AlCl_3 \cdot 6H_2O$.

(7) The oxidizing nature of nitric acid is likely to cause metallic corrosion problems in the presence of even small amounts of chlorides unavoidably introduced from a variety of sources.

(8) Environmental control problems include the elimination of nitrate losses to groundwater and removing NO_x from stack gases to meet environmental requirements.

2. 1. 2 Aluminum from Clay via Hydrochloric Acid Extraction - Evaporative Crystallization

(1) The process has been expressly designed for U. S. clays which are readily soluble in hydrochloric acid after an activating calcination and which have high ratios of acid-soluble alumina to acid-soluble metallic oxide impurity contents in the entering clay. The process can accommodate, with only minor increases in processing costs, reasonable amounts of silica and other acid-insoluble impurities which reduce the grade of many otherwise good U. S. clays. It can accommodate, with modest increases in processing cost (because of the nature of the iron rejection process employed), clays containing somewhat increased amounts of acid soluble iron. Processing costs will also increase with increasing ratios of acid soluble alkali and alkaline earth metal oxides to acid soluble alumina in the entering clay.

(2) Hydrochloric acid as a primary extractive reagent is likely to remain stable in cost. In addition, Cl_2 employed to oxidize ferrous iron to the ferric state eventually reports as makeup HCl. It is possible, especially with some raw materials, that this latter source could provide all required makeup HCl.

(3) Hydrochloric acid is chemically stable under all process conditions. HCl vapor produced by thermal decomposition of $AlCl_3.6H_2O$ may be recovered by condensation/absorption in water. Equilibrium partial pressures of HCl over dilute solutions of HCl are low, simplifying the recovery of HCl diluted with inert gases.

(4) A significant breakthrough in the use of hydrochloric acid as a leaching reagent is the recent availability of a solvent extraction system for iron removal which permits production of alumina with a satisfactory iron content. This method enjoys the advantage of using very dilute HCl to strip the iron from the loaded organic solvent.

(5) Only one hydrate, $AlCl_3 \cdot 6H_2O$, is formed upon crystallization of aluminum chloride from aqueous solution. This hydrate does not melt in its water of crystallization and requires only approximately 2/3 the heat for decomposition as is required for $Al(NO_3)_3 \cdot 9H_2O$.

(6) One advantage of the $AlCl_3 \cdot 6H_2O$ crystallization system is that sufficiently pure crystals can be precipitated from aqueous solutions containing some dissolved metallic chloride impurities. This in part is because most metallic elements, with the exception of alkalis, alkaline earths, and aluminum, tend to form soluble anionic chloride complexes in the presence of high aqueous chloride concentrations. For these reasons it is expected that only a single crystallization of the $AlCl_3 \cdot 6H_2O$ will be required with only a modest crystallizer bleed stream for soluble impurity control. Optimization of the crystallizer process section would require a considerable amount of additional study prior to design of a demonstration scale plant.

(7) The endothermic decomposition of $AlCl_3 \cdot 6H_2O$ may be carried out by direct contact between hot combustion product gases and the crystals undergoing decomposition. However, the presence of combustion product gases in admixture with the gaseous products of the decomposition increases the cost of equipment required for subsequent condensation of acid, and economically limits the concentration of the recovered acid to approximately 20% HCl. Additionally, in recent years the cost of clean fuel for the $AlCl_3 \cdot 6H_2O$ decomposition has risen dramatically in comparison with the cost of other fuels such as coal which are suitable energy sources only when the combustion products do not come into direct contact with the product alumina.

A considerable amount of further study and pilot scale development work would be required prior to the design of a cost-effective direct fired thermal decomposition process section.

(8) The 20% HCl recovered in the acid condenser is not suited to washing $AlCl_3 \cdot 6H_2O$ crystals because of their substantial solubility in acid of this concentration. Condenser acid to be used for crystal washing would require fortification to approximately 35% HCl.

(9) In the evaporative crystallization process all of the water in the leach liquor must be vaporized. This results in a considerably higher evaporation load compared to the HCl process using HCl gas sparging to promote crystallization.

(10) This process has the advantage of simpler technology in the salt decomposition phase.

(11) Its most important disadvantages in comparison with HCl leaching--HCl gas induced crystallization--indirect fired-decomposition are the higher evaporation requirement and the questionable future availability of a clean fuel for the direct-fired thermal decomposition step.

2.1.3 Alumina from Clay via Hydrochloric Acid Extraction - HCl Gas Induced Crystallization (Base Case)

(1) Process characteristics 1 through 6 inclusively, as listed under 2.1.2 HCL-Evaporative Crystallization, apply equally to this process. It is however expected that impurity rejection discussed under number 7 of that process will be improved by the employment of HCl-induced crystallization, since the formation of soluble impurity metal chloride complexes is enhanced in the presence of hydrochloric acid and because the ionization of small amounts of H_3PO_4 and H_2SO_4 expected to be present will be suppressed in the presence of HCl. The crystallization step has been demonstrated successfully; however further pilot scale study will be required before the design of a demonstration plant scale HCl-induced crystallization section be undertaken with confidence.

(2) After the crystallization step, the crystals of $AlCl_3 \cdot 6H_2O$ are separated from the mother liquor. This mother liquor is recycled to the leach step as liquor and does not go through the vapor phase as with the evaporative crystallization process. This method reduces the amount of evaporation required in this process compared to the HCl process using evaporative crystallization.

(3) This process requires HCl gas of at least 95% concentration for precipitation of $AlCl_3 \cdot 6H_2O$. The most practical way to produce this gas in the required amount is partial condensation of vapor rich in HCl and containing at most only small amounts of non-condensibles. This, in turn, requires that at least 90% of the thermal decomposition of the $AlCl_3 \cdot 6H_2O$ be accomplished without mixing the HCl/H_2O gaseous decomposition products with combustion products.

An extensive program of development effort to obtain design information must be carried out before the design of a demonstration scale, indirectly fired decomposer can be undertaken with confidence. However, there is reason to believe the design and construction of such equipment is possible. It is believed that the required equipment has been designed and constructed and is operating in France.

(4) To reduce the impurities in the product alumina the $AlCl_3 \cdot 6H_2O$ crystals must be washed free of mother liquor. The 35% hydrochloric acid is used for this purpose because of the low solubility of the crystals in this concentration. The 35% HCl can be produced by partial condensation of the gases leaving the indirect-fired decomposer.

(5) The HCl induced precipitation technique may be employed to minimize alumina losses in the bleed stream. Subsequently, distillation in the presence of a high concentration of waste chlorides should permit almost complete recovery of HCl in the bleed stream.

(6) The condensation of acid in the absence of inerts and exothermic operation of the primary crystallizer permits recovery of heat at temperatures high enough to be useful in evaporation or distillation, with the possibility of some reduction in the total process heat requirement.

(7) The primary disadvantage of this process is the requirement for development of indirectly fired decomposition equipment. Since questions of long term availability and added cost of clean fuel may eventually require the development of an indirectly heated decomposer capable of firing with coal for any acid process, this disadvantage may be short-term only.

2.1.4 Alumina from Clay via Sulfurous Acid Extraction

(1) Sulfur dioxide is a gas exhibiting only limited solubility in water; in addition, sulfurous acid is a weak acid. The consequences are:

(a) Pressurized leaching of calcined clay for a relatively long period of time is necessary to secure even a comparatively low alumina extraction.

(b) The alumina concentration of the leach acid solution is comparatively low.

(c) Most of the sulfurous acid section of the process must be operated under elevated pressure.

(2) The relative instability of aluminum sulfite permits the hydrothermal precipitation of alumina trihydrate which is advantageous. However, the sulfurous acid process section offers no means of separating iron or other impurity metals in solution, and even the separation of silica is incomplete. Hydrothermal precipitation of first a basic sulfite and then the trihydrate occurs in the presence of at least a part of these impurities. Consequently, no way is known to produce alumina trihydrate via sulfurous acid extraction that is pure enough to meet reduction-grade specifications without subsequent purification by means of a modified Bayer process.

(3) Sulfur in aqueous solutions as $SO_3^=$ dissociates to sulfate and sulfur relatively easily. In practice, this occurs during autoclaving. These chemical reactions cause substantial sulfur losses, processing difficulties in the Bayer refining section, and environmental control problems.

(4) Energy requirements are relatively high because of the need for two processes--a sulfurous acid process plus a modified Bayer process. The main energy users are the sulfurous acid autoclaving sections.

(5) The equipment required to put all of the alumina into solution twice, once in H_2SO_3 and once in NaOH, results in high capital cost.

(6) The process as defined discharges a large waste stream in the form of the mother liquor from the crude alumina trihydrate filtration. This stream most likely contains sulfur in various forms and would be an environmental problem.

2.1.5 Alumina from Anorthosite via Lime Sinter Process

(1) Anorthosite was originally attractive as a possible alumina source, because enormous reserves exist and because it is reasonably high in alumina grade. However, approximately

two units of limestone must be provided for each unit of anorthosite to make sinter feed, with the result that the total amount of sinter feed per unit of alumina produced becomes quite large. The quality of the limestone is also very important.

(2) Both the limestone and anorthosite must be very finely ground and proportioned with great accuracy to secure a satisfactory sinter; the grinding is energy intensive and the accurate blending difficult.

(3) The sintering process is very energy-intensive.

(4) It is very questionable whether decrepitation ("dusting" of the sinter into fine particles) can be secured by controlled cooling of the sinter on an industrial scale. Fine sinter particle size is required for leaching of the alumina values.

(5) There is no known practical solution to the problem of gelation, the possibility that solids undergoing leaching or settling may set up into a hard, concrete-like mass.

(6) It is questionable whether alumina of reduction-grade quality can be manufactured.

2.1.6 Alumina from Alunite/Reduction Roast - Bayer Extraction

(1) Mine-run alunite ore is low grade with respect to alumina, requiring the processing of at least eight units of ore per unit of alumina.

(2) The key front-end step, reduction roasting, appears capable of removing by reduction under optimum conditions only about 85% of the SO_4 associated with alumina. Even under these conditions a substantial fraction of the alumina is rendered caustic-insoluble.

(3) Unreduced sulfate associated with aluminum must be removed by leaching with dilute KOH or NH_4OH. K_2SO_4, originally a part of the alunite structure, is removed in the same leach.

(4) The process of solfataric alteration of feldspathic rocks, which creates alunite, is likely to create kaolinic clay and reactive silica in close association with it. Alumina and soda losses as

desilication product in the modified Bayer section of the process may be considerably higher than the values used in preparing the operating cost estimates. It may be difficult to make product specifications due to possible problems in desilicating the pregnant liquor adequately.

(5) The process as discussed here produces three products, namely alumina, potassium sulfate and sulfuric acid, all of which must either be marketed or disposed of economically.

(6) Known reserves of alunite are small in comparison with reserves of alumina in other nonbauxitic aluminous materials and are very restricted in geographic location.

TABLE 2-1

PROCESS ENERGY COMPARISON

	HNO_3	HCl Evap.	HCl Sparging	H_2SO_3	Anorthosite	Alunite
Net Heat to Process*	37.04	31.42	23.52	28.16	61.90	26.12
Gross Fuel*	46.90	32.63	27.36	37.45	61.90	29.33
% of Gross Fuel						
from Coal	87%	38%	66%	72%	94%	87%
from Fuel Oil	13%	62%	34%	28%	6%	13%

*As million Btu/T Al_2O_3. Net Heat to Process defined as total of all heat delivered to process stream including loss from process equipment. Gross Fuel defined as the total fuel burned and includes inefficiencies in steam generators, distribution losses, etc.

2.2 ECONOMIC COMPARISON OF THE SIX PROCESSES

Tables 3-1, 3-2, and 3-3 in section 3 compare the operating and capital costs for five processes against the base case, HCl/Clay with gas induced crystallization. This section of the report discusses the cost differences between each process and the base case as shown in Tables 3-1, 3-2, and 3-3. Only the significant differences in cost are discussed here.

Minor variations in ore cost between the four clay processes arise from differences in extraction efficiencies and alumina losses. The cost of alunite ore is considerably higher than for clay, largely because of greatly increased usage despite savings in overburden handling costs. The cost of anorthosite ore is less than for the base case clay process despite increased usage and certain other costs, because there is virtually no overburden to be handled in the anorthosite case.

2.2.1 Base Case: Alumina from Clay via Hydrochloric Acid Extraction - HCl Precipitation

The base case has the lowest operating and capital costs among the six processes for several reasons.

(1) The leach liquor evaporation load is relatively low due to recycling 26% HCl crystallization mother liquor back to leaching.

(2) The cost of ore and other reagents is generally lower than for other processes.

(3) The crystallization step is based on HCl gas sparging and has no evaporative load.

(4) The heat of decomposition of $AlCl_3 \cdot 6H_2O$ is relatively low compared to the nitrate, but higher than $Al(OH)_3$.

(5) 90% of the decomposition is done by indirect heating permitting the use of coal, which is cheaper than oil.

(6) The indirectly heated calcination facilitates the subsequent condensation of the decomposition off-gases due to the absence of fuel combustion products, resulting in considerable cost savings.

(7) The iron removal step is relatively simple and effective. This is equally true for both HCl processes.

2.2.2 Alumina from Clay via Nitric Acid Process

2.2.2.1 Comparison of Operating Costs to Base Case: Table 3-1

(1) Reagent Costs

Reagent costs for this process are $21.65 per ton of alumina greater than the base case. The reason for this difference is the relatively high usage of nitric acid by this process in its assumed form. Nitrate losses occur in the solvent extraction section and in waste solids washing. An additional nitrate loss results from decomposition of nitrate and NO_x to elemental N_2 at elevated temperatures during the decomposition of $Al(NO_3)_3 \cdot 9H_2O$. The cost of nitric acid is expected to increase in the future with the cost of ammonia, which is expected to increase with probable escalation of hydrocarbon feedstock costs. Nitrate losses in the thermal decomposition section possibly could be reduced, but an extended development effort would be required.

(2) Utilities

Utility costs are $23.03 per ton of alumina greater than the base case. Almost all of this is due to the greater fuel requirement for the HNO_3 process.

The major components of this greater fuel requirement are:

(a) the thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ which requires approximately 50% more heat per unit of alumina than is required for $AlCl_3 \cdot 6H_2O$.

(b) A relatively high steam load is required for leach liquor evaporation and for regenerating the HCl used in iron removal.

(3) Labor, Supplies, and Other

These three items are all higher for the nitric acid process relative to the base case. Maintenance labor and materials, and taxes and insurance, which compose part of these three items, have been estimated as a fixed percentage of the capital cost, and the capital cost for this process is considerably higher than the base case.

2.2.2.2 Comparison of Capital Costs to the Base Case: Table 3-2

The total plant capital costs are $289.73 per annual short ton greater than the base case.

Equipment costs for the salt decomposition system in the nitric acid process are more than double that for the base case. One reason is that provision must be made for the transfer of approximately 50% more heat than in the base case. Another reason is that the nitrate system uses the dense fluid bed mode, with lower gas velocities, while the chloride decomposition system can use an expanded bed mode with higher gas velocities. This effect plus higher gas evolution from decomposition of the $Al(NO_3)_3 \cdot 9H_2O$ necessitates the use of more fluid beds for the nitric acid process.

The steam plant costs are about twice that for the base case because of the need for a large amount of steam to regenerate HCl used in iron removal and because of substantial process steam evaporation requirements.

2.2.3 Alumina from Clay via Hydrochloric Acid Extraction - Evaporative Crystallization

2.2.3.1 Comparison of Operating costs to Base Case: Table 3-1 Utilities

The cost of utilities is $19.45 per ton greater than the base case for the following reasons.

(a) The use of 20% acid for leaching in this process, as compared with the use of 26% leach acid in the base case, increases the evaporation required to bring the leach liquor to saturation with respect to $AlCl_3$.

(b) In this process, as defined, all of the mother liquor from the crystallization stage must be vaporized. In the base case the mother liquor becomes leach acid without vaporization and is recycled directly to leaching. This difference results in the use of considerably more steam in the HCl evaporative crystallization process.

(c) The evaporative crystallization approach employs direct-fired thermal decomposition of the $AlCl_3 \cdot 6H_2O$. Oil has therefore been assumed to be the source for 100% of the energy requirement for the thermal decomposition as compared with only the last 10% in the base case. The added cost of oil in lieu of coal for 90% of the thermal decomposition energy requirement plus the cost of the added evaporation are responsible for the higher cost of utilities for this process in comparison with the base case.

If the $AlCl_3 \cdot 6H_2O$ decomposition system were converted to the indirect-fired mode it would be possible to save about $6 per ton of alumina in fuel costs. Conversion, if the technology were available, is estimated to add approximately $30 million to the capital cost for this section. For this reason, simply changing the calcination mode does not appear worthwhile, and in fact the indirect decomposition mode becomes advantageous only when incorporated in the HCl gas induced crystallization process as defined in the base case.

Additional opportunities exist for small reductions in utility costs through the development of less energy intensive methods of dealing with the iron extract from solvent extraction and of treating the crystallizer bleed stream, or by engineering the use of reclaimed heat for these requirements and/or for evaporation. Engineering the use of reclaimed heat will however be more difficult for this process than for the base case, because of the presence of inerts in the acid condensation feed which constitutes the main potential for recovery of waste heat.

2.2.3.2 Comparison of Capital Costs to the Base Case: Table 3-2

Capital costs for the HCl-evaporative process are the second lowest at $124.82 greater than the base case. Reasons for the differences are:

(1) Evaporation requirements to bring the purified leach liquor to saturation are substantially higher in the evaporative crystallization process than in the base case with a consequent increased capital requirement.

(2) The capital requirement for the crystallization section of the evaporative crystallization process is more than double that for the base case due to the large amount of evaporation required in this section and the large volume of vapor to be removed and condensed. In the base case there is no evaporation in this process section and only a relatively small amount of heat is rejected.

(3) The salt decomposition section for this process requires only about one-third the investment required for the base case because of provision in the base case for a large amount of corrosion-resistant heat transfer surface and a molten salt heating and circulating system.

(4) Acid recovery, in contrast, requires in this process a capital investment approximately four times that for the base case. The increase is due to the large amount of inert combustion product gases mixed with the hydrochloric acid to be condensed.

(5) The investment required in the steam plant for the evaporative crystallization process is almost double that for the base case because of the greater evaporation load.

2.2.4 Alumina from Clay via Sulfurous Acid Extraction

2.2.4.1 Comparison of Operating Costs to Base Case: Table 3-1

(1) Reagent Costs

One would expect sulfurous acid to be an inexpensive leaching reagent. Unfortunately, sulfur in the +4 valence state may be oxidized or reduced easily. Both of these processes occur, and the sulfur so inactivated must be replaced at substantial cost.

The process requires makeup caustic for the Bayer section, and this requirement combined with makeup sulfur brings the total primary reagent cost to a figure substantially higher than for the base case. Usages of these reagents have been extensively studied in the past, and there is believed to be little potential for any substantial reduction.

(2) Utilities

Utilities costs for this process are higher than the base case because of the need for large amounts of steam in the autoclaving sections of the sulfurous acid process. In addition, energy is required for the Bayer plant section of this process which has no equivalent in the base case.

(3) Labor and Other

These costs are higher than the base case because the maintenance and taxes component of these costs is based on equipment costs which are considerably higher for this sulfurous acid process.

2.2.4.2 Comparison of Capital Costs to the Base Case: Table 3-2

This process has the highest capital costs of all six processes at $512.94 greater than the base case. The main reasons for this difference are:

(1) Fifteen hours holding time under pressure are required to extract a reasonable amount of alumina from clay. This requires a very large and costly volume of pressurized reactors.

(2) The process requires both a sulfurous acid extraction plant and a modified Bayer plant to produce a suitable product which increases equipment requirements greatly.

(3) A sulfurous acid preparation system is included in the plant cost.

2.2.5 Alumina from Anorthosite via Lime Sinter Process

2.2.5.1 Comparison of Operating Costs to Base Case: Table 3-1

(1) Reagent Cost

The anorthosite-lime sinter process converts all calcium in the anorthosite to a calcium silicate and most of the aluminum to a calcium aluminate. The limestone requirement for this is high, i.e., 2 tons of limestone per ton of anorthosite, resulting in a reagent cost considerably higher than for the base case.

(2) Utilities

The cost of utilities for the anorthosite process are $43.09/ ton alumina higher than the base case.

A substantial amount of electrical power is required in the anorthosite-lime sinter process for the grinding of anorthosite ore and limestone, but the overwhelmingly dominant cost element is coal for the sintering operation. There is little prospect for any substantial reduction of this requirement.

2.2.5.2 Comparison of Capital Costs with the Base Case: Table 3-2

Capital costs for the anorthosite process are second highest in the group of processes compared.

The mining capital cost shown for the anorthosite process is based on the capital requirements for quarrying both anorthosite and limestone. The large capital costs are due to the mining operations to produce the two materials and the large amounts of both that are required to produce a ton of alumina.

Both the anorthosite and the limestone must be finely ground, precisely blended, and then sintered at high temperature for a considerable period of time. The resulting sinter must be cooled at a carefully controlled rate to produce a crystalline phase transformation which, in turn, will cause decrepitation into a fine powder. After alumina is leached from this very large mass of solids, the solids are washed prior to disposal. The leach liquor, must be desilicated, carbonated, thickened, classified, and then filtered to obtain alumina trihydrate. The numerous process steps, the large mass of solids involved, and low alumina concentrations in leach liquor result in a high process plant capital cost.

The waste disposal capital cost for this process is the highest of the group because of the addition of large quantities of limestone to the process. This results in the largest solid waste residue load of all the processes.

2.2.6 Alumina from Alunite/Reduction Roast - Bayer Extraction

2.2.6.1 Comparison of Operating Costs to the Base Case: Table 3-1

(1) Reagent Costs

Reagent costs for the alunite process are very high at \$64.38/ton of alumina greater than the base case for the following reasons.

(a) Caustic potash for leaching unreduced sulfate associated with aluminum is by far the largest single reagent cost item in the manufacture of alumina from alunite via reduction roasting. It is possible in further development of the process that a way may be found to more effectively reduce sulfate associated with alumina without affecting so severely the subsequent solubility of the alumina in caustic; but the probability of this is not considered high in view of the large amount of previous work having this goal. Alternatively, NH_4OH may be used to solubilize the unreduced sulfate, but in this case either a mixed $(NH_4)_2 SO_4 K_2SO_4$ must be marketed or NH_3 must be regenerated by adding lime with subsequent rejection of $CaSO_4$. Neither approach is attractive, and a major reduction in the cost of reagent for dealing with unreduced sulfate is believed unlikely.

(b) A second major reagent cost is that of makeup caustic soda for the Bayer processing section. A small amount of caustic soda is lost with the product alumina. A larger amount is lost even after careful washing of the large amount of solid waste remaining after alumina extraction, but by far the largest amount is lost by reaction with reactive silica and kaolin in the ore.

(2) By-Product Credit

The alunite process is the only one in the group which produces products other than alumina. For every ton of alumina produced one ton of sulfuric acid and 0.73 tons of potassium sulfate are also produced. There may be some difficulty in selling the large quantities of by-products produced. However, this study assumes that all the sulfuric acid can be sold in the southwestern U. S. and that the potassium sulfate can be sold as fertilizer. See section 3, Tables, for more details on cost development.

2.2.6.2 Comparison of Capital Costs with the Base Case: Table 3-2

Capital costs for this process are third highest in the group.

The processing of alunite requires capital provision for a large number of process steps including a sulfuric acid plant, a potassium sulfate plant, and a modified Bayer plant. These operations are relatively large scale, because the entering ore is low grade with respect to alumina. The Bayer process section is required to leach and then wash a much larger amount of solids/unit alumina than is the case in a Bayer plant operating on bauxite because of the low alumina content in the feed to the Bayer section when alunite is the raw material. Extra provision must be made for desilication. The low alumina content in the ore, a relatively low overall alumina extraction efficiency, and the number of steps required to separate the components of the ore result in a process plant capital cost much higher than the base case.

2.2.7 Review of Combined Capital and Operating Costs

Table 3-3 in the next section of the report combines the effects of capital and operating costs to develop one number by which the relative economics of the six processes can be judged. The table shows that, taking the net present value approach, and using a 10% discount rate, the processes would be rated in the following order:

1. HCl - Gas Sparged Crystallization
2. HCl - Evaporative Crystallization
3. Alunite
4. Anorthosite
5. Sulfurous Acid
6. Nitric Acid

The last three processes are very close in cost and could be ranked equal fourth.

If a 15% discount rate is assumed, the order changes with nitric acid becoming fourth, slightly ahead of anorthosite and sulfurous acid.

3. TABLES FOR COST COMPARISONS

3.1 OPERATING COST COMPARISON TABLE 3-1

3.1.1 Method Used to Develop Operating Costs

Section 3.1 presents operating cost comparisons for all six processes considered. The comparative costs are presented as the difference, in cost per ton of alumina produced, between each process and the "base case." The HCl/Clay process using HCl gas sparging to precipitate salt is used throughout as the base case since it has the lowest total operating cost per ton of product.

The operating costs are grouped into six cost elements; a seventh element is listed for by-product credits. The first element is "Ore Cost." Unit prices for ore are based on direct and indirect mining costs including labor, repair and maintenance supplies, overhead, royalty payments, and preproduction expense. Not included are depreciation, taxes, insurance, and certain overhead functions provided by the process plant organization. All ore-mining costs are calculated on a directly comparable basis. The unit cost of clay is identical in all clay cases. Mine-to-plant haul distances is assumed to be five miles for all ores. The cost of overburden removal is significant only for clay.

Each of the six processes is dependent on an acid or base to extract the alumina from the ore. The cost differential for these materials is reflected in the "Reagents" element. Unit costs have been obtained from potential suppliers, with the exception of limestone for the anorthosite process which is priced on the basis of mining it within five miles of the plant. Material usages have been based on the process material balance. Freight effects are considered only to the extent that alunite and anorthosite plants have been assumed to be West of the Rockies and all the clay process plants near Augusta, Georgia.

TABLE 3-1

OPERATING COST COMPARISON
500,000 TON/YR Al_2O_3

Operating Cost Difference, \$/Ton Al_2O_3	HNO_3	HCl Evap.	HCl Sparging*	H_2SO_3	Anorthosite	Alunite
Ore (Excluding Mining Capital)	.38	.37	Base Case	2.74	-4.28	5.38
Reagents (Acids & Bases)	21.65	.87	Base Case	5.44	10.43	64.38
Utilities (Oil, Coal, Power, Water)	23.03	19.45	Base Case	16.37	43.09	.01
Labor (Operating, R & M, Supervision, Administration)	5.80	1.88	Base Case	5.42	.79	3.11
Supplies (R & M, Operating, Processing)	13.31	2.67	Base Case	-.22	-4.05	-1.71
Other	3.40	1.51	Base Case	6.11	3.44	3.58
Subtotal	67.57	26.75	Base Case	35.86	49.42	74.75
By-Product Credit (K_2SO_4 & H_2SO_4)						-62.63
Total Difference, \$/Ton Al_2O_3	67.57	26.75	Base Case	35.86	49.42	12.12

Note: Costs shown represent difference between each process and the base case. Positive values represent higher costs; negative values represent lower costs. Costs are calculated at 500,000 ton/yr rate and reflect differences per ton Al_2O_3 produced.

*Sparging: HCl gas-induced crystallization

The third element of comparative operating cost is "Utilities." The differences shown indicate primarily the various energy requirements for the individual processes. In all cases the cheapest practical fuel commensurate with the required product purity has been used. Therefore, coal is the fuel of choice except when direct contact with the product is required in the acid processes. In those situations requiring contact, No. 6 fuel oil is used. Natural gas is not specified for any process as the availability is questionable. A single unit cost and grade has been used for coal and fuel oil in all cases. Fuel usages are based on the process energy requirements with comparative allowances for efficiency and heat losses.

In the "Labor" element of operating cost repair and maintenance (R & M) labor cost is the most variable. R & M has been calculated as a percentage of direct process plant capital with a higher rate for highly corrosive processes (HNO_3 & HCl) and a lower rate for non-corrosive processes (alunite and anorthosite) with sulfurous acid at an intermediate level. The operating labor requirements have been compared by estimating the manpower requirements for each section of each process. Supervision and administration are calculated assuming a fixed administrative staff size and a constant ratio of supervisors to operating labor and R & M labor.

The "Supplies" element contains repair and maintenance materials, operating supplies such as gas and oil, small tools, filter cloth, etc., and processing supplies such as flocculant, lime, chlorine, etc. Most of the differences between processes arises from R & M materials which are based on capital cost and process corrosivity.

The "Other" element represents taxes and insurance. It is calculated as a fixed percentage of capital for all processes. No differences are implied based on location.

The alunite process produces sulfuric acid and sulfate of potash as by-products. Since H_2SO_4 production is large (1,500 ton/d) and there is minimal demand in Utah, the acid would have to be either shipped out or converted to another product on site. For this study, it is assumed H_2SO_4 would be shipped to Houston, Texas and sold on a freight-equalized basis. Sulfate of potash also presents a marketing problem. The proposed plant would be the largest producer of this product in the U. S. Since demand for the product is seasonal and depends on the state of the agricultural economy, problems of moving the entire plant output are to be expected. For this study, an intermediate price between today's prices for sulfate of potash and muriate of potash has been assumed. For simplicity, the full sales price for the potash is given to the plant as a credit with no deductions for selling trade allowances, G & A, and overhead costs, although some costs would be incurred for the functions.

The comparative total operating cost difference represents a totaling of the seven elements of differential cost. These values represent the total additional cost of producing one ton of alumina for each process compared to the base case.

3.2 CAPITAL COST COMPARISON TABLE 3-2

3.2.1 Method Used to Develop Mining Capital Costs

Mining capital costs in table 3-2 have been assembled for each ore based on the required annual tonnage. Overburden removal is required for clay and alunite, but not anorthosite and limestone. Similar or identical equipment has been used throughout and equipment costs are based on recent user experience. Equipment operating capacities have been obtained by reducing manufacturer's design ratings by an appropriate amount based on recent user experience. The individual ore capital estimates include both mobile equipment and fixed facilities such as shops, utilities, roads, and fuel storage. Separate mining facilities have been provided for anorthosite and limestone, both of which are used in the anorthosite process. The values shown in the capital cost table represent the difference in required mining cost between each process and the base case process expressed as dollars per annual ton of alumina.

3.2.2 Method Used to Develop Process Plant Capital Costs

The process plant capital costs in table 3-2 have been developed from the conceptual block flow diagrams and material balances found in section 4. Informal specifications for major equipment have been provided to multiple competing vendors for obtaining up-to-date cost data and availability of equipment for the first half of 1977.

Values for process equipment represent the differences of installed equipment cost between each process and the base case as dollars per annual ton. Other direct capital cost differences for foundations, structures, piping, utilities, electrical, etc., are developed from

TABLE 3-2

CAPITAL COST COMPARISON
500,000 Ton/Yr Plant

Capital Cost Difference, \$/Aton*	HNO_3	HCl Evap.	HCl Sparging**	H_2SO_3	Anorthosite	Alunite
Mining Capital Difference	-0-	-0-	Base Case	-0-	40.74	.08
Process Plant Capital Differences						
Process Equipment	108.21	43.54	Base Case	196.69	151.20	93.57
Other Direct Capital (Foundations, Structures, Piping, Utilities, Electrical, Etc.)	122.33	58.41	Base Case	217.88	81.74	149.25
Indirect Capital and Freight	52.51	22.52	Base Case	94.48	53.14	55.44
Waste Disposal Capital Difference	3.00	-0-	Base Case	-0-	36.20	1.00
Working Capital Difference	3.68	.35	Base Case	3.89	6.68	7.24
Total Capital Cost Difference, \$/ATon	289.73	124.82	Base Case	512.94	369.70	306.58

Note: Costs shown represent difference in capital dollars between process and base case. Positive values represent higher capital requirements. Costs are calculated based on plant sized to produce 500,000 ton/yr of alumina, and reflect differences in capital spending for each ton of alumina capacity.

*\$/Aton: Dollars/Annual Ton of Al_2O_3

**Sparging: HCl gas-induced crystallization percentage factors based on experience in alumina and other metallurgical processes. Indirect capital cost differences include such items as salaries, burden, overhead, personnel expenses, and office expenses. Freight costs have been identified with indirect costs.

The process plant capital costs excludes contingencies, escalation, and owners' costs.

3.2.3 Method Used to Develop Waste Disposal Capital Costs

The capital cost differences shown for waste disposal in table 3-2 represent cost differentials for facilities to impound solid residues remaining after alumina removal from the ores. In all cases except anorthosite, the mined out area created by ore removal has been used for mud disposal. Due to the large volume of solids with anorthosite, levee construction is required. Generally the capital costs are for pumps, piping, sumps, and electrics necessary to deliver slurry to the disposal area and to recycle liquor back to the plant.

3.2.4 Method Used to Develop Working Capital Costs

Working capital cost differences shown in table 3-2 represent the differences in costs required to maintain adequate inventories of materials, supplies, and product. Materials inventories are set at 10 days, supplies at 30 days, except oil at 10 days and coal at 45 days, and product at 5 days. An exception was the alunite byproduct sulfate of potash for which 45 days is used due to the highly seasonal nature of demand. All items are charged at their cost of production or purchase.

3.3 ECONOMIC COST COMPARISON TABLE 3-3

3.3.1 Methods Used to Compare the Combined Effects of Capital and Operating Costs for the Six Processes

In table 3-3, the difference between the Net Present Value of the total cashflow for each process and the base case process is shown at two discount rates. The Net Present Value for each process has been calculated from the cashflow for each project year 1 through 30 including both capital and operating expenditures. Plant construction is assumed to require 3 years. Additional capital is to be spent

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every 5 years for waste mud impoundment facilities. Operations are assumed to begin in year 4 and remain at capacity through year 30. Working capital is to be invested in years 3 and 4 and recovered in year 30. Depreciation is according to current tax law and sum-of-the-years' digits depreciation rate is used. A tax rate of 50% is used in conjunction with a 10% investment tax credit. No inflationary escalation has been considered. Finally, to assume a 30-year life for the project, the values shown in the table represent the incremental total project cost for capital plus operating costs in 1977 dollars for either a 10% or a 15% cost of capital.

TABLE 3-3

CAPITAL PLUS OPERATING COSTS
500,000 Ton/Yr Al_2O_3

	HNO_3	HCl Evap.	HCl Sparging*	H_2SO_3	Anorthosite	Alunite
Net Present Value of Incremental Cumulative Cash Flow ($ millions)						
10% Discount Rate	-195.0	-79.6	Base Case	-191.5	-190.6	-98.0
15% Discount Rate	-150.2	-62.0	Base Case	-168.9	-154.0	-90.6

Incremental net present values are shown in millions of dollars of all project costs for 30 years, including capital and operating expense, discounted to the present at rate shown. Negative values indicate a more costly project in current dollars.

*Sparging: HCl gas-induced crystallization

4. APPRAISALS OF SIX PROCESSES

4.0 Raw Materials Background: Clay, Anorthosite, Alunite

The technical appraisals for the six processes described in this section are based on using clay, anorthosite, or alunite as the ore raw material. These minerals are available domestically in sufficient quantities and high enough assays to warrant the evaluation of processes for extracting cell grade alumina from them.

4.0.1 Clay as a Raw Material

Very large reserves of clay suitable for the production of alumina exist within the contiguous 48 states.

The primary mineral is kaolinite, the alumina content of which may be rendered almost completely acid-soluble by calcination at 1100° - 1500°F. The calcine is actually a better acid extractive process feed than the above analysis might indicate because the minor constituent metal oxides tend to be in part derived from residual micas and feldspars in the clay. Metal oxides combined in these accessory minerals are only partially soluble in acid under the extraction conditions employed by the processes under discussion, thereby improving the soluble alumina to impurities ratio in the process liquor stream. Iron, unfortunately, occurs primarily in the clay either as free Fe_2O_3 or as a replacement for aluminum in the kaolinite lattice. In either case it is acid soluble.

The abundance of kaolinic clay, its high grade with respect to alumina, the ease with which the alumina may be rendered acid soluble, the possibility of rejecting the major unwanted constituent of the clay (silica) without reagent consumption, and the high ratio of acid soluble alumina to impurities combine to make kaolinic clay a preferred raw material, after bauxite, for the extraction of alumina.

4.0.2 Anorthosite as a Raw Material

The crystalline rock anorthosite is the calcium-rich end member of the soda-lime feldspar series which varies isomorphously in all proportions from albite, $NaAlSi_3O_8$, to pure anorthite, $CaAl_2Si_2O_8$. It is estimated that approximately 1.6×10^{11} tons of alumina, or much more than the total contained in all other minerals considered to be potential sources of alumina in the U.S., are available in reserves of anorthosite.

Thus it may be observed that anorthosite is a potential source of virtually unlimited amounts of alumina, provided that the problem of separating alumina from the primary impurities silica, lime, soda, and potassium can be solved on a basis competitive with the extraction of alumina from other less plentiful nonbauxitic materials. The difficulty of extracting alumina from anorthosite is increased by the fact that in anorthosite the alumina is in very strong chemical combination with the other constituents.

Secondary but major raw materials which have been employed in nearly all past efforts to extract alumina from anorthosite are limestone and coal. The U. S. is plentifully endowed with both of these materials, so no detailed discussion of them will be undertaken here. It must be noted, however, that high-quality deposits of both of these materials have appreciated greatly in value in recent years, and the cost of transporting them has also increased greatly.

4.0.3 Alunite as a Raw Material

Alunite is a naturally occurring basic sulfate of potassium and aluminum made basic by the presence of alumina trihydrate in its molecule. The chemical formula of alunite may be written:

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2Al_2O_3 \cdot 6H_2O.$$

In naturally occurring deposits varying amounts of sodium substitute for potassium. Alunite appears to be formed as a result of solfataric action of hot acid waters upon feldspathic rocks. Much of the silica content of the original rock remains in admixture with the alunite; and it is important to note that although much of the silica may be in the form of quartz, some of it may be in the form of opal, which is chemically reactive to alkali. Slightly different conditions of alteration of the original rock may result in the gradation of alunite in an ore body into kaolinic clay, which is another mineral containing alkali-reactive silica.

Alunite has been used by various civilizations at least since the time of the Roman Empire as a source of potassium alum, but known deposits of it were two small to be considered as an important potential source of alumina. In 1970, however, a large

4.0.2

deposit of alunite was discovered in Southwestern Utah. It is estimated that at least 100 x 10^6 tons of alumina, and possibly considerably more, are in place in alunite ore analyzing 5-20% Al_2O_3.

4.0.3

4.1 TECHNICAL APPRAISAL: ALUMINA FROM CLAY VIA NITRIC ACID EXTRACTION

4.1.1 Summary and Conclusions

The process being evaluated for the manufacture of reduction-grade alumina from clay via nitric acid extraction is illustrated in summary form on the following page. It includes the following steps:

(1) Calcination of the clay.

(2) Leaching of the calcine at atmospheric pressure at boiling with slightly greater than the stoichiometric amount of nitric acid.

(3) Separation, washing, and rejection to disposal of the acid-insoluble component (primarily silica) of the clay.

(4) Removal of dissolved iron from the leach liquor by a solvent extraction process which regenerates and recycles the organic extractant.

(5) Concentration by evaporation of the leach liquor from which the iron has been removed.

(6) Cooling the hot concentrated solution of aluminum nitrate to selectively crystallize $Al(NO_3)_3 \cdot 9H_2O$, thereby separating the aluminum from certain dissolved minor constituent metals.

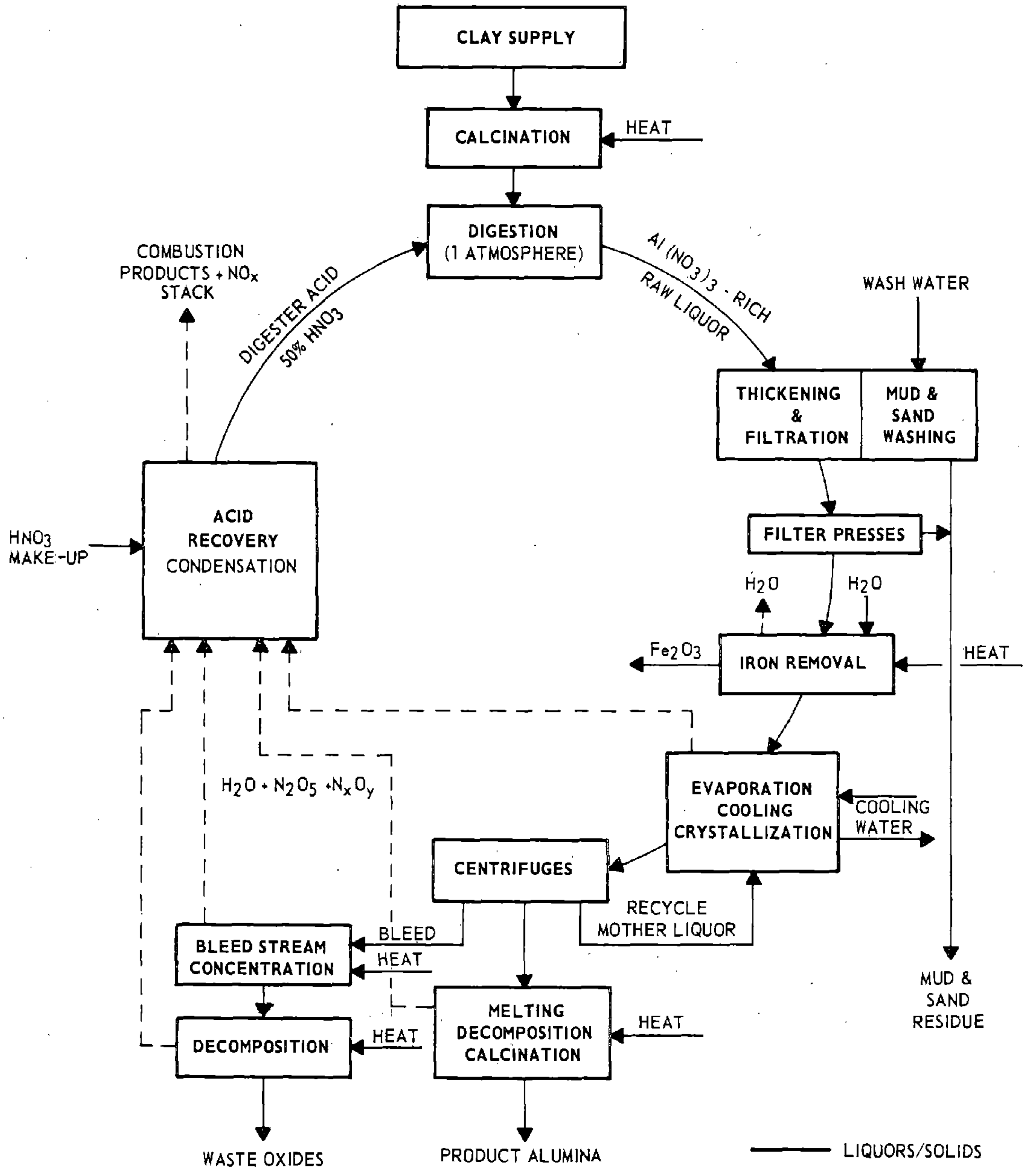
(7) Thermally decomposing the $Al(NO_3)_3 \cdot 9H_2O$ to obtain the product alumina.

(8) Withdrawing and thermally decomposing for nitrate recovery a fraction of the mother liquor remaining after crystallization of $Al(NO_3)_3 \cdot 9H_2O$. The withdrawal is made to control the concentration of dissolved impurity metals present in the crystallizer. Decomposition of this stream produces waste metal oxides which are sent to disposal.

(9) Recovering, for recycle, by condensation and absorption, nitric acid vapors and nitrogen oxides produced in thermal decomposition or elsewhere in the process.

FIGURE 4-1-1

ALUMINA FROM CLAY VIA HNO_3 EXTRACTION



It is highly probable that alumina meeting reduction-grade chemical purity specifications can be manufactured from clay via nitric acid extraction. The estimated net thermal energy requirement to the process is 37.0 x 10^6 Btu/ton alumina, possibly reducible by further study and engineering design for heat recovery. Approximately 600,000 Btu/ton of clean fuel such as oil will be required for the final stage of thermal decomposition. Any fuel including coal could be used as fuel for steam generation and for indirectly fired decomposition.

Nitric acid losses are substantial, and there is some doubt whether makeup acid will be obtainable at acceptable cost at the time use of the process would be desired.

Corrosion of metallic materials of construction, in particular that caused by the interaction of even small amounts of chlorides with nitric acid and acidic nitrate solutions, is expected to present severe difficulties. Exclusion of chlorides to the required degree is considered to be nearly impossible.

Two technological problems require solution before design of a demonstration plant can be undertaken with a reasonable probability of successful operation. These are:

(1) Operation of the thermal decomposition and acid recovery steps must be further studied and interrelated to obtain maximum recovery of nitric acid with minimum introduction of water or steam. Methods of carrying out the thermal decomposition employed by the Idaho National Engineering Laboratory (INEL) and by the Arthur D. Little Company incurred economically disadvantageous losses of nitrate by decomposition to N_2. An accurate material balance for the thermal decomposition-acid recovery sections in the design finally chosen must be developed to make certain that an unacceptable loss of nitrate either as oxides of nitrogen or elemental nitrogen is not incurred in these sections of the process.

(2) A means must be developed for treating the large volumes of waste water from chloride and nitrate wash steps in solvent extraction. These solutions cannot be expelled into the environment as is. These streams constitute a significant nitrate loss.

Energy and capital required for whatever mode of treatment is chosen must be added to the process totals.

In addition, three other process sections of (1) crystallization, (2) solid-liquid separation, and (3) clay calcination would benefit from the availability of additional engineering design information. However, additional information on these latter three is not as critical as for the former three technological problems.

4.1.2 Background

The first reported serious investigation of the use of nitric acid in the manufacture of alumina took place in the early years of the twentieth century in Norway where nitric acid was manufactured by the Birkland-Eyde process employing then-surplus hydroelectric power, and where there are no deposits of bauxite. Natural advantages of working in the nitrate system include the following:

(1) Iron has a very low solubility in solutions of aluminum nitrate in which there are somewhat less than three moles of nitrate per mole of aluminum. However, insofar as can be determined, the solubility of iron in basic nitrate solutions is still high enough to preclude meeting current reduction grade standards for the product alumina without multiple crystallizations of $Al(NO_3)_3 \cdot 9H_2O$. Partly for this reason the recently developed solvent extraction method for the removal of iron appears to have superseded the employment of basic nitrate solutions for iron removal. However, this method has problems in additional nitrate losses, waste solution disposal, and the hazard of possibly mixing chloride and nitrate in the primary process liquor in the event of operational upsets. The process being evaluated herein operates with a slight excess of acid in relation to alumina and allows the iron to go into solution.

(2) Aluminum nitrate in the presence of water is decomposed by heat at fairly low temperatures to the oxide. This decomposition is quantitative at higher temperatures with the result that no foreign substance is introduced into the reduction cell due to incomplete decomposition.

(3) Most, but unfortunately not all, of the nitrate volatilized during decomposition can be recovered as acid by direct condensation. Most of that not recovered in this manner may be recovered by installation of nitrogen oxide scrubbing/absorption equipment.

(4) Nitric acid is a strong acid. The solubility of silica in it is small, and silica precipitated upon the decomposition of meta kaolin by nitric acid tends to be nongelatinous and relatively easy to separate from the resulting solution.

(5) Aluminum nitrate, like other nitrates, is quite soluble in water, and its solubility increases sharply with increasing temperature. Up to almost 200 gpl alumina may therefore be carried in hot solutions, and process liquors are relatively free from scaling problems.

(6) Some purification may be achieved in the fractional crystallization of $Al(NO_3)_3 \cdot 9H_2O$.

The use of nitric acid received further impetus from development of the Haber process for ammonia and from the development of corrosion resistant alloys for apparatus construction. Intensive investigation in Germany prior to World War II culminated in the "Nuvalon" process, which was tested at what today would be considered a semicommercial scale. This process employed less than stoichiometric amounts of acid in relation to clay in order to minimize iron and titanium solubility. Leaching was done at elevated temperature under pressure in order to maximize alumina recovery in the presence of the reduced amounts of acid.

During the period following World War II much was learned from the U.S. Atomic Energy program about the application of aqueous nitrate systems to hydrometallurgical processes. The mature development of the use of low-cost U.S. natural gas as a feed stock in the manufacture of ammonia reduced the cost of nitric acid to what was probably an all-time low in relation to the cost of other acids. Finally, the development of liquid ion exchange technology for the separation of iron from aluminum made possible abandonment of pressurized leaching while improving product alumina quality along with yields of alumina from the clay. These factors together with the need to develop a process for the manufacture of alumina from domestic resources probably have been responsible for development of the process which is the subject of this evaluation.

The evaluation is based primarily upon data derived from USBM RI 6431 and TMS Paper No. A 74-49 by S. V. Margolin and R. W. Hyde. Other information has been supplied by the A. D. Little Company and by the Idaho National Laboratory (INEL).

4.1.3 The Process

4.1.3.1 Summary

Clay entering the process is first calcined to chemically activate it, to remove free and combined water, and to destroy organics. It is next leached with a slight excess of nitric acid, dissolving aluminum and small amounts of iron, alkali and alkaline earth metal oxides. Waste solids, primarily silica, are separated from the leach liquor in a thickening and washing operation and the washed solids sent to disposal. Iron is removed from the combined liquor and washings by solvent extraction. The liquor after iron removal is concentrated by vacuum evaporation and then subjected to cooling crystallization to produce crystalline $Al(NO_3)_3 \cdot 9H_2O$. The crystals are recovered by centrifuging and washed with concentrated nitric acid. A portion of the mother liquor is withdrawn for the control of soluble impurities other than iron, but most of the mother liquor is recycled to evaporation. Decomposition of the aluminum nitrate to alumina is accomplished by melting the crystals in their water of hydration and then spraying the melt into a heated fluidized bed of alumina particles previously prepared by the decomposition process. Approximately 90% of the decomposition is accomplished in this first stage. The decomposition is completed in a second stage where the solid particles are heated to a higher temperature in the presence of steam. Acid vapors and oxides of nitrogen from both stages are recovered for recycle in a condensation/absorption system.

4.1.3.2 Calcination

Clay from the mine may be dried if necessary to render it amenable to materials handling and particle size control, following which it is sent to covered storage. Clay is withdrawn from storage and crushed/agglomerated as necessary. It next goes to calcination, which may be direct fired with any conventional fuel including powdered coal.

All acidic leaching processes for the recovery of alumina from clay--with the conditional exception of sulfuric acid leaching--require calcination of the clay for 0.1 to 2 hrs in the temperature range 1200-1500°F in order to render the clay suitably reactive to the leaching acid. The reaction is:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{\Delta H} Al_2O_3 \cdot +2SiO_2 + 2H_2O \uparrow$$

Kaolinite Meta Kaolin

The literature indicates that all of each clay particle being calcined must reach temperature within the above limits in order for the alumina to be rendered acid soluble but that conversion of alumina to the acid soluble form is very rapid once the specified temperature range is reached. The required residence time in calcination is therefore largely determined by the size of particles calcined and by the rate of heat transfer to individual particles. Calcined clay particles may be held within the specified temperature range for reasonable periods of time without loss of alumina reactivity, but heating them above this range will cause rapid deactivation of the alumina. Calcination also removed free and combined water and destroys any organic materials which may be present in the clay as mined.

If coal is used for calcination, small particles of ash which may remain in the calcine are not expected to interfere with subsequent processing, because this processing must, in any case, provide for separation of impurities that might be introduced through the leaching of ash and because the particles of ash are expected to be rendered largely inert by the high temperature they will selectively attain during combustion.

An oil-fired rotary kiln is the accepted method of accomplishing this calcination and in practice requires approximately 5.5×10^6 Btu/ton alumina. The technology for the calcination and the associated materials handling is fully developed. A potentially better method of calcining the clay--but which is not yet developed for this application--is the employment of a fluid bed calciner. This technique could offer the following advantages.

(1) Reduction in thermal energy requirements by up to 1.5×10^6 Btu/ton alumina.

(2) Better control of and a more uniform calcination of the clay, making possible a higher alumina extraction from the clay.

(3) Delivery to the leaching process of a product calcine having an optimum particle size distribution for leaching and the subsequent solid-liquid separation, with savings in dilution water introduced during washing and capital costs.

(4) Possible capital savings in calciner cost due to decreased residence time.

The above comments apply to all acid processes involving clay calcination. The major question about the use of fluidized solids techniques for calcination is whether the physical properties of the clay will permit the use of this technique without the generation of excessive amounts of fines having an uncertain degree of calcination. USBM has scheduled some pilot-scale fluidized solids clay calcination tests which are expected to make possible a decision on the feasibility of the fluid bed alternative.

4.1.3.3 Leaching

The primary leaching reaction is:

$$Al_2O_3 \cdot 2SiO_2 + 6HNO_3 \longrightarrow 2Al(NO_3)_3 \cdot 3H_2O + 2SiO_2$$

Meta Kaolin	Solution	Solution	Waste

The technology for leaching is well developed. It is expected that calcined clay and a small stoichiometric excess of acid will be simultaneously and continuously metered into the first of a series of covered, gently agitated tanks. These tanks can be of carbon steel construction with a polymeric lining to protect the steel, and with an inner lining of acid resistant brick. The leaching reaction will be sufficiently exothermic to maintain the tanks at boiling. Some vapors comprising a mixture of HNO_3, H_2O, and NO_x arising from the boiling liquor will be conducted to a condenser. The HNO_3 and H_2O will be returned to the leaching system. The NO_x must be subsequently recovered in an absorber.

It is expected that 95% of the alumina content, about the same percentage of the iron content, and lesser percentages of minor constituent metal oxide impurities in the clay will dissolve during a 4-hour leach with 105% of the stoichiometric acid requirement at temperatures of 240° -250°F. The amounts and percentages of minor constituent impurity metal oxides which dissolve will depend in part upon the mineralogy of the specific clay.

4.1.3.4 Solid-Liquid Separation

Undissolved solids in the slurry emerging from the leach must be separated from the leach liquor, washed as free as economically possible of adhering liquor, and then conveyed by some means to a tailings disposal area, which will probably be a clay pit in the vicinity where mining has been completed. The technology required for the engineering design of this operation is well known, provided that the following are known as well: the relative amounts of liquor and solids, the particle size distribution of the solids, their amenability to flocculation and the settling rate of the flocculated particles, the degree of dissolved solids recovery required, the density, and viscosity of the solutions. Enough is known about the properties of the residue and solution produced by nitric acid leaching of Georgia clay to make possible the preliminary engineering design of a multistage countercurrent decantation washing system.

Much work remains to be done on optimizing the residue solid-liquid separation operation. This will also require further study of leaching, because initial acid concentration, leach time, and even the manner in which the calcined clay and entering acid are initially mixed can influence the physical properties of the silica leach residue. The design of a leaching system tending to preserve the particle size distribution in a calcined feed clay of selected particle size distribution could permit the initial separation as sand of a substantial mass fraction of the silica. An effective flocculant could greatly reduce the required settler area. No problem appears to exist that would actually prevent operation of the process, but the amount of dilution water introduced to the process in actual operation could vary substantially from the figure given above, influencing both energy costs and the capital required for subsequent evaporation. There could also be a wide variation in the capital requirement for settler/filters.

4.1.3.5 Solvent Extraction

The U.S. Bureau of Mines and the A. D. Little Co. have proposed the removal of dissolved iron from the leach liquor by solvent extraction with a mixture of di-ethyl-hexyl phosphoric acid (DEHPA) and tri-butyl phosphate (TBP) in kerosene solvent. Stripping is accomplished by contacting the iron-loaded organic phase with hydrochloric acid. The iron passes back into the aqueous phase as an anionic chloride complex with simultaneous regeneration of the organic phase for recycle.

There is little doubt that the solvent extraction step will remove iron to produce a primary liquor stream meeting the iron specification, but some important technical problems with respect to this method of iron separation remain unresolved. The iron loaded into the organic phase actually coextracts some nitrate from the primary leach liquor. Aqueous hydrochloric acid is required for stripping, but chloride and nitrate ions must be kept separated in order to avoid their interaction which would result in loss of reagent together with severe corrosion problems. The iron-loaded organic phase must therefore be washed with water to ensure the complete removal of nitrate before contact with the hydrochloric acid stripping solution. Some residual iron in the stripped organic complexes with HCl and thereby carries some of the chloride into the organic phase. The regenerated organic must again be washed with water to remove this chloride and avoid carrying it back into the primary nitrate liquor stream.

These three aqueous streams represent important losses of nitrate, organic extractant, and alumina occurring in combinations which cannot be discharged to the environment. A possible use for the first nitrate wash solution may be to wash waste solids.

The iron-bearing, used HCl solution is first treated with H_2SO_4 and then evaporated to produce a waste $FeSO_4$ sludge and recover most of the HCl.

The second chloride wash solution, because of its chemical nature, will be difficult to process for recovery of its constituents, and the method of doing so is not known. The reprocessing/utilization of these streams is an important problem that requires solution before nitric acid could be employed commercially in the extraction of alumina from clay.

The use of this solvent extraction also presents a hazard in that an operational upset could cause the introduction of chloride into the acidic primary nitrate liquor with consequent severe metallic corrosion problems.

The alternative to removal of iron by solvent extraction is to leach the calcined clay with a substoichiometric quantity of nitric acid at elevated temperature and pressure to repress the solubility of iron while maximizing that of alumina, or to add back a portion of substoichiometric nitrate solution prepared by distillation to a quantity of leach liquor prepared by stoichiometric leaching at atmospheric pressure and then autoclave the mixture for a period of time to precipitate iron. It is presumed that the German investigators, since the solvent extraction technique was not known at the time of their work, thoroughly studied both variations of substoichiometric iron rejection before choosing pressurized leaching. In either case, lengthy pressurized treatment of the primary liquor stream at elevated temperatures, with the attendant technical problems and costs, is required. Unfortunately, insofar as can be determined, the achievable iron rejection also is inadequate in terms of present day Fe_2O_3 specifications in the product alumina without resorting to multiple crystallizations of the $Al(NO_3)_3 \cdot 9H_2O$. Consequently, solvent extraction was the iron removal method chosen for the process being evaluated. Data on iron removal via solvent extraction was available from the miniplant.

4.1.3.6 Evaporation

Evaporation under vacuum removes approximately 2.7 mass units H_2O/unit product alumina. The condensate contains approximately 0.5% HNO_3. The technology of the evaporative process is well-known and should require very little additional development work.

4.1.3.7 Crystallization

The preceding vacuum evaporation yields a liquor which at temperatures lower than those prevailing in the evaporator is supersaturated with respect to aluminum nitrate. This liquor is cooled evaporatively in at least two stages of crystallization to prepare $Al(NO_3)_3 \cdot 9H_2O$. The crystals are recovered by centrifuging and then may be washed with 50% nitric acid. The

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used wash acid would go to leaching. The major part of the centrifugate is recycled to evaporation, but a fraction of it is diverted as a bleed stream in order to control the buildup of minor constituent metal nitrates. This bleed stream may, of course, be subjected to further evaporation and crystallization to reduce losses of $Al(NO_3)_3 \cdot 9H_2O$, the impure crystals so recovered being redissolved in the primary leach liquor. Subsequently, the bleed stream is processed for recovery of contained nitrate values.

A recent patent indicates that the amount of the bleed stream may be substantially reduced and final crystal purity improved by operating with a higher level of impurities in the crystallizer and producing slightly impure crystals. These crystals are then redissolved in pure water from which $Al(NO_3)_3 \cdot 9H_2O$ is recrystallized. The recrystallized material is washed with water, which is also used countercurrently to wash the crystals initially produced. This procedure is virtually certain to achieve both of the above objectives, but at a considerable cost for increased capital and energy for evaporation.

Results from the miniplant studies and the teachings of the patent referred to above suggest that the separation factor between aluminum and other metals is not high, although there is little doubt that the crystallization can be engineered to produce $Al(NO_3)_3 \cdot 9H_2O$ crystals of the required purity. Insufficient data is available in the published literature to evaluate the optimum number of crystallizer stages versus bleed stream losses, so for the purposes of Task I the process evaluated has been based upon the U.S. Bureau of Mines flowsheet employing a single crystallization stage and at the same size bleed stream as has been assumed in evaluating the hydrochloric acid processes. Additional crystallization studies would be required prior to a demonstration plant design to determine the optimum trade-off between crystal growth rate per unit crystallizer volume, crystal size, washing procedure and amount of wash liquid, the number of crystallizations, consequent evaporation, and the size of the bleed stream.

4.1.3.8 Decomposition

It is expected that $Al(NO_3)_3 \cdot 9H_2O$ crystals of requisite purity will be melted at 165°F in their water of crystallization. The resulting liquor will be sprayed onto existing alumina particles in a series of indirectly heated beds fluidized by recycled decomposition products, or by steam. The film of liquid acquired by any given particle in this rapidly circulating hot bed will decompose almost instantaneously to form an onion-skin-like layer of oxide containing only a fraction of the nitrate originally present. The amount of residual nitrate in the bed product is an inverse function of the temperature at which the bed is operated and the solids residence time.

In practice, in order to obtain the highest thermal efficiency and to minimize exposure of the nitric acid/nitrogen oxide vapors to high temperatures, the decomposition will probably be carried out stagewise with the solids subjected to increasing temperatures in succeeding stages as decomposition is carried to completion. It is expected that the final stage of decomposition will be carried out in a direct-fired fluid bed under slightly reducing conditions at 1,500°F to destroy the last traces of nitrate in the product alumina.

The idealized overall reaction for the decomposition is:

$$2Al(NO_3)_3 \cdot 9H_2O_{(l)} \rightarrow Al_2O_{3(c)} + 6HNO_{3(g)}\uparrow + 15H_2O_{(g)}\uparrow$$

The estimated net energy requirement for this reaction is approximately 20.8×10^6 Btu/ton alumina.

Some undesired gas phase reactions also occur to varying degrees dependent upon the temperature and the residence time of the gases within the decomposer, the composition of the gaseous phase, and possibly upon catalytic properties of the alumina itself or of metal surfaces within the decomposer.

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2$$

$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2$$

$$2NO \rightarrow N_2 + O_2$$

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

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The oxides of nitrogen are thermodynamically unstable at ambient temperature and at all temperatures encountered in the decomposer; if thermodynamic equilibrium was attained, decomposition to N_2 and O_2 would be virtually complete. Fortunately, the kinetics for decomposition reactions yielding the elements are such that only a small amount of decomposition to the elements normally occurs excepting at temperatures higher than those required for carefully designed decomposition. N_2O_5, NO_2, and NO also can be at equilibrium with each other, O_2, and H_2O. Increasing the temperature shifts these equilibria sharply in the direction of oxides with lower oxygen content whereas lowering it shifts the equilibria in the direction of the higher oxides/liquid acid. It is therefore desirable to operate the decomposer at the lowest possible temperature and with the shortest possible gas residence time to minimize the decomposition of nitric acid and any higher oxides of nitrogen, but it is also possible to reconstitute acid from NO and NO_2 in the presence of O_2 and H_2O in the acid condenser/absorber. N_2O_5 requires only the presence of H_2O.

Nitrogen oxides which have decomposed so as to form N_2O or N_2 cannot be reoxidized and recovered as acid in the condenser/absorber, and are irretrievably lost. N_2O usually does not form in the absence of a reducing agent, but small amounts of it formed by an unknown mechanism were observed in gases exiting a decomposer operated at 750°F by the Idaho National Engineering Laboratory (INEL). The decomposition of NO to N_2 is reported to be very slow at temperatures below about 1,200°F. Detection of the formation of N_2 is difficult, because it is inert and because under process conditions a substantial amount of N_2 derived from air is likely also to be present. The easiest way to detect loss of nitrate by decomposition to N_2 is usually by difference.

Hazen Research Inc. in an $Al(NO_3)_3$ decomposition test carried out at 1,000°F as part of the miniplant program was unable to account for 22% of the nitrate fed to decomposition. Unfortunately, the NO_x recovery/reconstitution system used during the Hazen test was inadequate so an accurate nitrogen balance around $Al(NO_3)_3 \cdot 9H_2O$ decomposition could not be developed from that work. Nitrate decomposition studies carried out by INEL at a somewhat lower temperature--but one still higher than would be used when one of the goals would be maximum nitrate recovery--did permit construction of a nitrogen balance. Calculations based upon gas analyses and other data obtained from INEL showed decomposition to N_2 and O_2 of approximately 14% of the nitrate fed to a decomposer operating at 750°F. A material balance for a decomposition process operating at 400°F showed the disappearance of 7.4% of the nitrate fed to decomposition. The evidence is quite strong that the decomposition of some nitrate to N_2 and N_2O does, in fact, take place. A possible explanation for the observation of larger losses of nitrate by decomposition to N_2 than would be expected from reported studies of the decomposition of nitrogen oxides is catalysis of the decomposition by the large mass of reactive alumina, or by metal surfaces present in the decomposer at any given time. Another possible explanation is a decomposition reaction mechanism which produces N_2 and O_2 directly. Some further reduction of nitrate loss to N_2 may be possible by careful engineering of the decomposition process or by means of some presently unknown technique, although 400°F for various reasons is probably close to the minimum temperature practical for industrial scale decomposition.

There is little doubt that $Al(NO_3)_3 \cdot 9H_2O$ melted in its water of crystallization can be decomposed to Al_2O_3 using fluidized solids techniques with indirect heating of the bed; INEL has already accomplished this at what would today be considered pilot scale. They operated a liquid NaK heat transfer system as a heat source for decomposition for approximately 40,000 hours with very little corrosion on the NaK side or other problems and also experienced no significant corrosion/erosion on the nitrate side of the heat transfer surfaces over the same period of time. INEL also solved successfully the problems of introducing a viscous liquid into the bed, and of controlling bed particle size.

The INEL effort was unconcerned about the recovery of nitrate. Required before the construction of a demonstration plant for the manufacture of alumina via nitric acid extraction from clay is the development of a decomposer-acid recovery design capable of producing reduction-grade alumina with an acceptable nitrate recovery, and verification of the cost, operability, and acid recovery for the design.

4.1.3.9 Bleed Stream Treatment

Filtrate from the recovery of $Al(NO_3)_3 \cdot 9H_2O$ crystals is saturated with respect to $Al(NO_3)_3$, which together with free HNO_3 comprises approximately 45% by weight of this stream. It is unfortunate that this is the least disadvantageous stream from which to withdraw the bleed stream taken for the control of soluble impurities other than iron, because taking the expected required amount of bleed will result in rejection along with impurities of a substantial amount of previously dissolved alumina. It is probable that further study of the crystallization and/or washing the product crystals with concentrated acid would provide the basis for reducing the size of the bleed stream while still meeting product specifications. The amount of reduction achievable and the effort required are unknown.

It is also probable that the amount of bleed stream taken relative to alumina production may be reduced when the raw material is a clay containing only very small amounts of acid soluble accessory minerals, or if the accessory minerals present are only slightly soluble in the acid. Conversely, the presence of acid soluble potassium in an accessory mineral would tend to increase the bleed stream requirement because the potassium specification for the product alumina is very low. The effect of accessory minerals in specific clays on the bleed stream requirement has not been studied to date although it is estimated that working with high-grade clay under optimum crystallizer conditions may permit a reduction in the bleed stream to 5% or less of the mother liquor. It may be economical to evaporate, cool, and possibly even chill the bleed stream to recover for recycle a fraction of its contained aluminum nitrate. Impure crystals so obtained would be redissolved in the primary liquor stream prior to evaporation. This has not been studied.

It is expected, in order to recover the contained nitrate values, that the bleed stream will be decomposed in a process and apparatus very similar to the one used for final product recovery. In this case a waste solid oxide will be produced suitable for disposal. The amount of bleed stream to be processed per unit of final product obviously will have an important bearing on total energy consumption per unit of final product. All of the comments in section 4.1.3.8 about further study of $Al(NO_3)_3 \cdot 9H_2O$ decomposition apply equally to decomposition of the waste stream.

4.1.3.10 Acid Recovery

Acid which is present in the vapor phase as HNO_3 may be recovered by simple condensation. Nitrate which has undergone decomposition to oxides of nitrogen will require a more complicated absorption system. The proportion of nitrate present in decomposer off-gases as HNO_3 will tend to increase as the temperature of decomposition is decreased and with increasing partial pressures of steam. The use of auxiliary steam will facilitate both decomposition and acid recovery, but will increase energy costs for provision of the steam and for later removal by evaporation of the added water. Thermal decomposition should be studied in conjunction with acid recovery to optimize these interrelated operations. It would be necessary to do this study before designing a nitric acid alumina demonstration plant.

4.1.4 Energy Requirements

The net thermal energy required by the process is summarized below. Gross fuel energy requirements will be somewhat higher.

Process Section	Btu x 10^6
Clay Calcination	5.5
Solvent Extraction Waste Stream Treatment	4.6
Evaporation	2.7
Primary Aluminum Nitrate Decomposition	22.7
Waste Nitrate Decomposition	1.5
	37.0

The energy requirement for clay calcination may be reduced somewhat from the tabulated value by employing fluidized solids rather than rotary kiln calcination, but development work is required. Coal may be used as the energy source with either method of calcination, but again with the requirement of some development work. The energy required for evaporation may be reduced to some extent if the leaching-solid-liquid separation system is studied further to optimize it, thus minimizing primary liquor dilution. Coal will probably be used to generate steam required for evaporation.

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The heat required for nitrate decomposition is by far the largest process energy input. Coal may be employed as fuel to supply the indirectly fired major part of the decomposition heat load. A relatively small amount of clean fuel will be required for the final direct fired, higher temperature, reducing calcination which removes the final traces of nitrate from the product alumina.

A substantial amount of heat may be recovered from the condensation of nitric acid vapors produced by aluminum nitrate and waste nitrate bleed stream decomposition. This heat may be used in evaporation although its utilization will require innovative engineering design effort. Such effort is expected to be worthwhile because utilization of this heat offers significant capital as well as operating cost savings.

The energy requirement for bleed stream treatment may vary from the estimated value in accordance with the amount of bleed actually required. This would be determined from sustained cyclic process operation.

4.1.5 Environmental Impact

The extraction of alumina from clay via nitric acid will require total impoundment of the waste solids from leaching in order to prevent loss to the environment of nitrates/nitric acid remaining in the waste solids which will be discarded. Spillage and dilute solutions of nitrates will require similar containment. It is possible that very dilute solutions of nitrates ultimately recovered from the drainage of waste solids or from other sources may be returned to the process as wash water, nitrogen oxide absorber water or in some other way. In some climates an excess of these solutions could be concentrated by solar evaporation in open ponds prior to return to the process.

Alternates include, but are not limited to, use of the waste nitrate solutions as agricultural irrigation water or reduction of the nitrate to elemental nitrogen by soluble organic materials such as methanol followed by disposition of the remaining water to the environment.

It is not possible, on the basis of presently available information, to design the optimum method of dealing with these solutions, because their amount and composition, as well as the climate of the plantsite, are not known.

A small amount of gaseous nitrogen oxides will be produced during leaching by the oxidation of ferrous to ferric iron. A much larger--but presently unknown--quantity of nitrogen oxides will be produced by nitrate decomposition. Under conditions wherein these oxides are not in admixture with large quantities of combustion gases, recovery of them by absorption employing known technology to meet existing environmental control standards is possible. It is not known but is doubtful whether a sufficient degree of recovery can be achieved at an acceptable cost of nitrogen oxides from decomposition that are mixed with combustion products.

4.1.6 Alumina Product Quality

There are no known published alumina analyses from a nitric acid extraction process operated under industrial conditions in accordance with the flowsheet being evaluated here, but product analyses from the miniplant operation give reason to believe that, with refinements in the process and some changes in materials of construction to avoid the presence of metallic corrosion products, reduction grade alumina chemical specifications can be met. As stated in a preceding section, the ratio of the bleed stream to primary alumina product required to meet reduction grade specifications when working with a specific raw material may vary.

The extent to which nitrate may be economically removed from the alumina product is not known. It is expected that any residual nitrate will be expelled upon addition of the alumina to the reduction cells. The presence of NO_x in the cell off-gases would require additional provision at the reduction plant for environmental control. Such provision would be costly.

4.1.7 Overall Comments

The following overall comments are offered in regard to the production of alumina from clay via nitric acid extraction:

(1) The price of ammonia used as the primary raw material in the manufacture of makeup nitric acid has escalated by a factor of at least 4 in the last 5 years. This escalation is due in large part to the decreasing availability and increasing cost of natural gas. It is a trend which can only continue.

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(2) The energy requirement for producing alumina via nitric acid extraction is relatively high. This is because:

(a) Aluminum nitrate nonahydrate forms in the crystallization step relied upon for rejection of impurity metals other than iron. Decomposition of the nonahydrate requires a large amount of heat.

(b) The chemical nature of the process requires that all of the water in which the aluminum nitrate is dissolved as it passes out of the leaching step must eventually be vaporized.

(c) Water must be added to the process in the absorption of nitrogen oxides and very probably in thermal decomposition to inhibit the decomposition of nitrate to nitrogen oxides. Any water so added is supplied as steam and then must subsequently be removed by evaporation.

(d) Hydrochloric acid solution used to regenerate organic solvent in iron removal is regenerated by sulfuric acid treatment followed by distillation. This distillation requires a substantial amount of energy.

(3) Environmental control will be relatively costly. The nitrate ion does not normally occur naturally in groundwater and is very undesirable even in extremely small concentrations. The oxides of nitrogen are undesirable air pollutants and are costly to control.

(4) The nitrate group is not stable under some conditions that cannot be avoided in the process, with the result that a fraction of the nitrate present decomposes to various oxides of nitrogen during the processing cycle. This acts to increase the process capital as well as energy requirements. Additionally, there will be in practice an unavoidable loss of nitrate by decomposition to the lower oxides of nitrogen and to elemental N_2. The amount of this loss has not been precisely established because the process has not yet been operated with a sufficiently accurate material balance. Such a loss could easily be large enough to have economic significance.

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4.1.8 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000 ton/d of alumina.

(2) The chemical analysis of the clay feed (dry basis) is as follows:

Al_2O_3	36.5%
Fe_2O_3	0.86
SiO_2	46.4
L.O.I.	13.54
Other*	2.7
Total	100.00%

*Other is primarily TiO_2

(3) The raw clay feed to the process contains 18.5% free moisture.

(4) A rotary kiln is used for the dehydration of the clay feedstock.

(5) There is a 1% dust loss (calcined basis) from the dehydration rotary kilns.

(6) 50% by weight nitric acid is utilized in the process (makeup acid and that recycled from the acid recovery section).

(7) 95% extraction efficiency of Al_2O_3 is achieved in the leaching step.

(8) 8.4% of "other" is solubilized in the leaching step.

(9) 67% of Fe_2O_3 is solubilized in the leaching step.

(10) The underflow from the settling and washing units contains 30% solids by weight.

(11) 1% of the soluble alumina is lost in the waste residues.

(12) The iron content in the pregnant solution from solvent extraction is reduced to about 0.001 g/l.

(13) Approximately 1.0% of the dissolved alumina is lost in the solvent extraction step.

(14) 1 ton/d of organic is lost in the solvent extraction step.

(15) 17% HCl by weight is used as the stripping acid in the solvent extraction section.

(16) Triple effect evaporators are used for the concentration of the main aluminum nitrate solution and the bleed stream of aluminum nitrate.

(17) The $Al(NO_3)_3 \cdot 9H_2O$ crystals from the centrifugation of the slurry of crystals will contain 5% liquor by weight.

(18) Fluid bed roasters are used to decompose $Al(NO_3)_3 \cdot 9H_2O$ for both the main and bleed streams.

(19) There is a 0.5% dust loss (calcined basis) from the final calcination of alumina.

(20) 98% decomposition of $Al(NO_3)_3 \cdot 9H_2O$ is achieved in the indirect thermal decomposition step.

(21) There is a 3% loss of nitrate as N_2 in the indirect thermal decomposition step.

(22) There is a 2% loss of nitrate as N_2 in the direct-fired product calciner.

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TABLE 4-1-1

ALUMINA FROM CLAY NITRIC ACID PROCESS DAILY THERMAL REQUIREMENTS FOR 1,000 TON/D Al_2O_3

	15 LB/IN² (GA) STEAM, M LBS (945 BTU/LB)	100 LB/IN² (GA) STEAM, M LBS (881 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
CLAY PREPARATION				
CALCINATION	–	–	5,491	–
LEACHING				
LEACHING CONDENSERS	–	–	–	2,171
CRYSTALLIZATION				
EVAPORATION (3-effect)	2,841	9	–	5,634
CRYSTALLIZERS	–	–	–	3,288
PRODUCT RECOVERY				
MELTING	–	1,484	–	–
FLUID BED DECOMPOSITION	–	–	20,819	–
CALCINATION	–	–	604	–
CONDENSERS	–	–	–	8,648
WASTE NITRATE RECOVERY				
EVAPORATION (3-effect)	102	9	–	210
MELTING	–	36	–	–
DECOMPOSITION	–	–	1,410	–
CONDENSERS	–	–	–	705
HCl REGENERATION				
DISTILLATION	–	5,198	–	–
CONDENSERS	–	–	–	8,109
TOTALS	2,943 (2,781 MM BTU)	6,736 (5,934 MM BTU)	28,324	28,766

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 37,039 MM BTU/D *OR* 37.0 MM BTU/TON Al_2O_3

Table 4-1-2 (Sheet 1 of 5)

Alumina from Clay/Nitric Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	1	2	3	4	5	6	7	8	9	10	11
Component											
Al_2O_3	1131	1131	12	1119	1119	56					
$Al(NO_3)_3$						4441	4397	4395	4351	6354	2153
$Al(NO_3)_3 \cdot 9H_2O$											7396
$AlCl_3$											
$Al(OH)_3$											
Fe_2O_3	27	27		27	27	9					
$Fe(NO_3)_3$						53	53	53			
$Fe(OH)_3$											
$FeCl_3$											
SiO_2	1436	1436	14	1422	1422	1422	12				
LOI	402	402	402								
H_2O	699	699	699			4736	6350	6353	6339	9437	6242
Other	84	84	1	83	83	83	7	6	6	73	73
HNO_3						185	183	183	229	3214	3214
N_2O_5											
HCl											
Organic											
CO_2											
O_2											
N_2											
H_2SO_4											
Total	3779	3779	1128	2651	2651	10985	11002	10990	10925	19078	19078

All units are in short tons per day

Table 4-1-2 (Sheet 2 of 5)

Alumina from Clay/Nitric Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	12	13	14	15	16	17	18	19	20	21	22
Component											
Al_2O_3			986		1000						36
$Al(NO_3)_3$						2003	150	150		150	
$Al(NO_3)_3 \cdot 9H_2O$	7396	7396	148								
$AlCl_3$											
$Al(OH)_3$											
Fe_2O_3											
$Fe(NO_3)_3$											
$Fe(OH)_3$											
$FeCl_3$											
SiO_2											
LOI											
H_2O	195	195		3326		5807	435	338	97	338	
Other	1	1	1		1	67	5	5		5	5
HNO_3	195	195		195		2990	224	221	3	221	
N_2O_5				3032							
HCl											
Organic											
CO_2											
O_2				73							
N_2				26							
H_2SO_4											
Total	7787	7787	1135	6652	1001	10867	814	714	100	714	41

Table 4-1-2 (Sheet 3 of 5)

Alumina from Clay/Nitric Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	23	24	25	26	27	28	29	30	31	32	33
Component											
Al_2O_3									5		
$Al(NO_3)_3$											
$Al(NO_3)_3 \cdot 9H_2O$											
$AlCl_3$											
$Al(OH)_3$											
Fe_2O_3											
$Fe(NO_3)_3$											
$Fe(OH)_3$											
$FeCl_3$											
SiO_2											
LOI											
H_2O	338		319	2821		854	2705	1851	63	76	4167
Other											
HNO_3	221		354	3732		2	5	3		76	4167
N_2O_5	114										
HCl											
Organic											
CO_2											
O_2					73				49		
N_2					26				17		
H_2SO_4											
Total	673	–	673	6553	99	856	2710	1854	134	152	8334

Table 4-1-2 (Sheet 4 of 5)

Alumina from Clay/Nitric Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	34	35	36	37	38	39	40	41	42	43	44
Component											
Al_2O_3	56			56							
$Al(NO_3)_3$	2066	2022		44		2		15			8
$Al(NO_3)_3 \cdot 9H_2O$											
$AlCl_3$											
$Al(OH)_3$								10			12
Fe_2O_3	9			9							
$Fe(NO_3)_3$	25	25						30			16
$Fe(OH)_3$								10			15
$FeCl_3$											
SiO_2	1410			1410		12					
LOI											
H_2O	1467	3081	3361	3598	17	10			3481	3481	
Other	76			76		1					
HNO_3	86	84		5						14	
N_2O_5											
HCl											
Organic							1	2811			2811
CO_2											
O_2											
N_2											
H_2SO_4											
Total	5195	5212	3361	5198	17	25	1	2876	3481	3495	2862

Table 4-1-2 (Sheet 5 of 5)

Alumina from Clay/Nitric Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	45	46	47	48	49	50	51	52	53	54	55
Component											
Al_2O_3											
$Al(NO_3)_3$		2	6			6		2			
$Al(NO_3)_3 \cdot 9H_2O$											
$AlCl_3$											
$Al(OH)_3$		12						12			
Fe_2O_3											
$Fe(NO_3)_3$		10	6			6		10			
$Fe(OH)_3$		15						15			
$FeCl_3$											
SiO_2											
LOI											
H_2O	2073	2073		6108		6108	1	205	1869	204	195
Other											
HNO_3											195
N_2O_5											
HCl	422	417	5			5		51	366	56	
Organic			2811		2810	1					
CO_2											
O_2											
N_2											
H_2SO_4							51	51			
Total	2495	2529	2828	6108	2810	6126	52	346	2235	260	390

4.1.9 Equipment List

ALUMINA FROM NITRIC ACID/CLAY PROCESS

Clay Preparation Area

Belt conveyor, under wobbler feeder and primary crusher
Truck dump hopper
Wobbler feeder and hoppers from truck dump
Primary crusher and chutes
Belt conveyor primary crushers to stockpile
Belt conveyor and distributors for stockpile
Stockpile, enclosure, dust collection system, and reclaim system
Wobbler feeder from stockpile
Belt conveyor stockpile to hammermills
Hammermills and hoppers
Belt conveyor hammermills to elevator
Bucket elevators from secondary crusher
Vibrating screens, chutes, and covers
Roll compactors with covers
Belt conveyor compactors to elevators
Belt conveyor screens to raw clay surge bin
Raw clay surge bin
Weigh belt feeders
Belt conveyors raw clay surge bin to kilns
Rotary kilns
Apron feeders with covers
Calcine bucket elevators
Calcine vibrating screens and chutes
Calcine cage mill grinder with covers
Calcine apron feeder with cover
Bucket elevator to calcine storage bins
Calcine storage bins concrete
Weigh belt feeders to leaching
Belt conveyors to leach tanks
Dust collection systems

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EQUIPMENT LIST (Cont)

Leaching, Thickening, Filtration Area

Leach tanks with draft tube (lined)
Calcined clay feeders
Leach tank agitators
HNO_3 vapor condensers
Leach tank recirculating pumps
Leach tank discharge pumps
Condensed HNO_3 pumps
Sand thickeners (covered and lined)
Thickener underflow pumps
Thickener overflow pumps
Sand thickener rakes
Sand washers (covered and lined)
Sand washer rakes
Sand washer underflow pump
Sand washer overflow pump
Wash waste water tank (lined)
Wash waste water tank pump
Flocculation feed hoppers and feeders
Flocculation mix tank
Flocculation mix tank agitator
Flocculation transfer pump
Flocculation storage tank
Flocculation solution pump
Sump relay tank (lined)
Sump relay tank pump
Wash water storage tank (lined)
Wash water storage tank pump
Wash water relay tank (lined)
Wash water relay tank pump
Filter press
Repulpers
Collecting sluice
Vibrating screen
Press cake tank (lined)
Repulped slurry pump
Spent filter aid dumpers
Filtrate tank (lined)
Filtrate pump

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EQUIPMENT LIST (Cont)

Filter aid storage tank
Filter aid conveyor, weigh feeder
Filter aid slurry tanks
Filter aid slurry tank agitators
Filter aid slurry pumps
Filter liquor pumps

Solvent Extraction HCl Stripping Area

Pregnant liquor surge tank (lined)
Pregnant liquor surge pumps
Kerosene unloading pump
Kerosene storage tank
Kerosene blending pumps
DEHPA unloading pump
DEHPA storage tank
DEHPA blending pumps and heaters
Solvent blend tank
Solvent blend tank agitator
Solvent surge tank
Solvent surge pumps
Mixer-settler tanks (lined)
Mixer-settler head tanks
Pumping-mixing turbines and baffles
Unwashed loaded solvent pumps
Unwashed loaded solvent storage tank
Unwashed loaded solvent storage tank pumps
Loaded solvent pumps
Loaded solvent storage tanks
Loaded solvent storage tanks pumps
Spent HCl pumps
Unwashed solvent pumps
Unwashed solvent storage tank
Unwashed solvent storage tank pumps
Solvent pumps
Solvent blend tank pumps
Settler overflow
Solvent extraction pump

EQUIPMENT LIST (Cont)

Solvent sump skimmer
Solvent sump transfer pump
Skimmed solvent pumps
Raffinate pumps
Raffinate storage tank
Raffinate storage tank pumps
Fume collectors
Spent HCl solution static mixer
HCl recovery evaporation reboilers
HCl recovery surge tanks (glass lined)
HCl recovery surge tank agitators
HCl recovery condensers
HCl slurry pumps
HCl transfer pumps
HCl storage tank (lined)
100,000 gal H_2SO_4 storage tank
H_2SO_4 unloading pumps
H_2SO_4 transfer pumps

Heat Interchange, Evaporation, Crystallization, Centrifuging Area

Heat interchange system (flash tanks, heat exchangers, pumps, and barometric condenser
Heat interchange Hotwell and cover (lined)
Heat interchange Hotwell pumps
Product evaporators triple effect, (pumps, heaters, preheaters, vapor piping, surface condenser and barometric condenser)
Product evaporator Hotwell and cover (lined)
Product evaporator Hotwell pumps
Crystallizers (tanks, vaporizers, barometric condenser, steam ejectors, circulating pumps and transfer pumps)
Crystallizer Hotwell and cover (lined)
Crystallizer Hotwell pumps
Crystallizer dump tank
Crystallizer dump tank pumps
Crystallizer dump tank heat exchanger
Centrifuge feed slurry tanks
Centrifuge feed pump

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EQUIPMENT LIST (Cont)

Mother liquor recycle tanks
Centrifugation purge pumps
Evaporator recycle feed pumps
Cyclone receiver tank
Cyclone classifiers
Centrifuges
Centrate collection tanks (lined)
Centrate tank pumps
Centrifuge discharge screw conveyor
Bucket elevator
Purge nitrate storage tanks (lined)

Product Melting, Decomposition, Calcination Area

Wet crystal surge tanks (lined)
Wet crystal surge tank screw conveyors
Melt tank bucket elevator
Product melt tank
Product melt tank agitators
Product melt tank steam coils
Product melt tank pumps
Product decomposers
Decomposer cyclones
Decomposer heat exchangers
Heat transfer systems
Recycle gas blowers
Product decomposer discharge screw conveyors
Surge bin feed conveyor
Surge bin bucket elevator
Calciner feed surge bin
Surge bin recirculating screen conveyor
Product calciner feed screw conveyors
Product calciner system
Alumina conveyors
Alumina distribution conveyors
Alumina product silos concrete
Heat transfer system coal pulverizers
Heat transfer system ash handling
Heat transfer system precipitators
Heat transfer system SO_2 gas scrubbers

EQUIPMENT LIST (Cont)

Purge Nitrate Evaporation, Melting, Decomposition Area

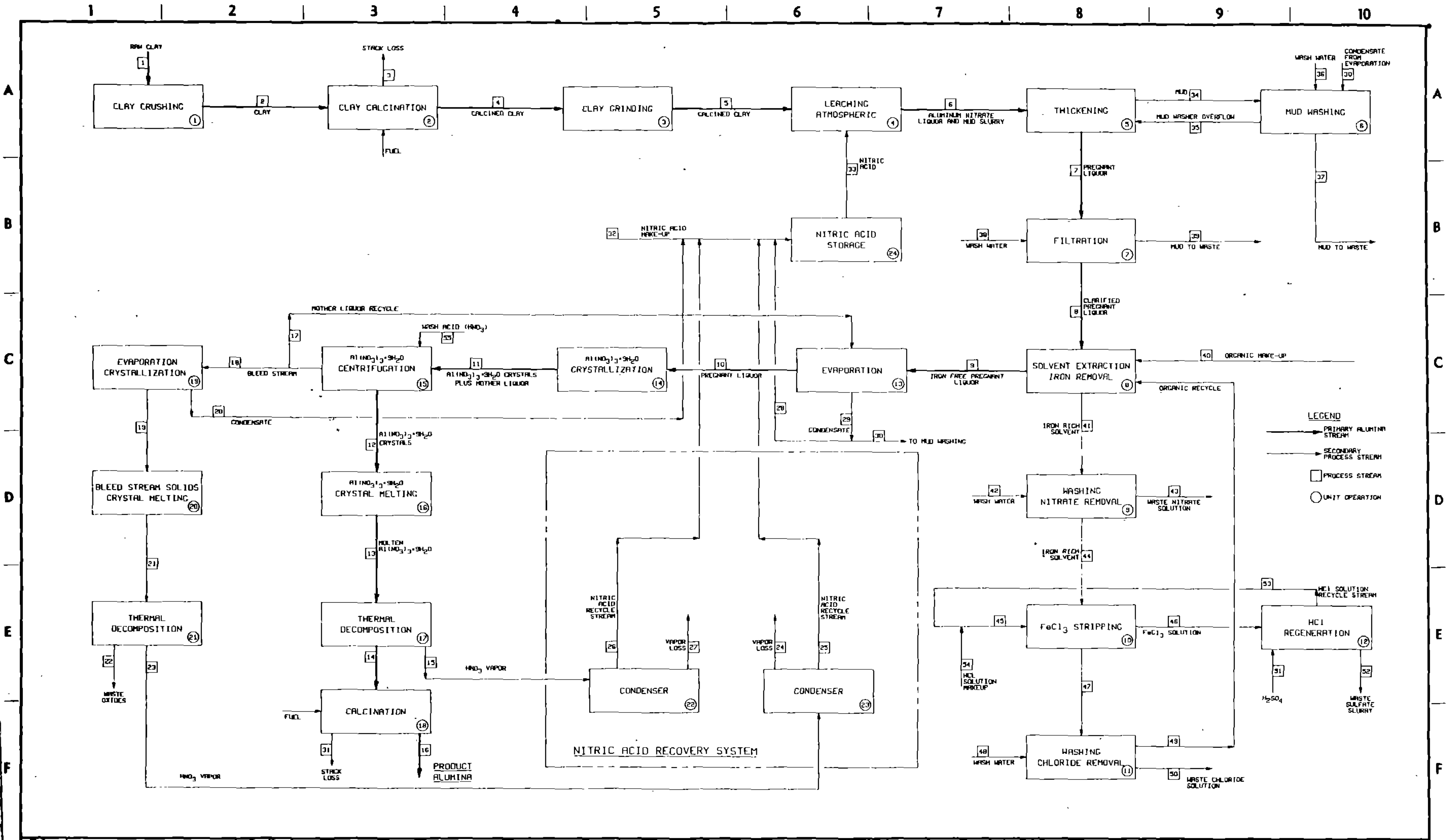
Purge nitrate triple effect evaporator (circulating pumps, preheaters, vapor piping, barometric condenser)
Purge nitrate evaporator Hotwell and cover (lined)
Purge nitrate evaporator Hotwell pumps
Purge nitrate evaporator transfer pumps
Purge nitrate melt tanks
Purge nitrate melt tanks agitators
Purge nitrate melt tanks heating coils
Purge nitrate melt tanks pumps
Purge nitrate decomposers system
Purge nitrate slurry tank
Purge nitrate slurry pumps
Purge nitrate slurry agitators
Purge nitrate recycle blowers
Purge nitrate venturi scrubbers
Purge nitrate cyclone separators
Purge nitrate recirculation pumps
Purge nitrate liquor cooler
Purge nitrate heat transfer system coal pulverizer

NO_x Removal and Acid Recovery Area

Venturi gas scrubbers
Cyclone separators
Gas scrubber circulating pumps
Gas scrubber circulating coolers
Catalytic combustor system
HNO_3 storage tanks
HNO_3 recovery product pumps
HNO_3, 50% leach feed pumps

Utilities

Steam plant and auxiliary systems
Cooling towers and auxiliary systems



NO. | DATE | REVISION | APP. | APP.

NOTES

FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-1-2

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-1-1

DESCRIPTION | COST ACCOUNT

CONSTRUCTION APPROVAL

APPROVAL | DATE

SCALE: | DATE

DESIGNED BY

DRAWN BY ADS

CHECKED BY

APPROVED BY

APPROVED BY

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO. [illegible]

ALUMINA FROM CLAY
NITRIC ACID PROCESS

JOB No. 76161-001 | DWG. No. FIGURE NO. 4-1-2 | REVISION 0

4.2 HCl/CLAY: EVAPORATIVE CRYSTALLIZATION

4.2 TECHNICAL APPRAISAL: ALUMINA FROM CLAY VIA HYDROCHLORIC ACID EXTRACTION-EVAPORATIVE CRYSTALLIZATION

4.2.1 Summary and Conclusions

The process being evaluated for the manufacture of reduction-grade alumina from clay via hydrochloric acid extraction with evaporative crystallization includes the following steps illustrated by the attached flowsheet:

(1) Calcination of the clay.

(2) Leaching of the calcine at atmospheric pressure at boiling with slightly greater than the stoichiometric amount of approximately 20% hydrochloric acid.

(3) Separation, washing, and rejection to disposal of the acid-insoluble component (primarily silica) of the clay.

(4) Removal of dissolved iron from the leach liquor by a solvent extraction process which regenerates and recycles the organic extractant.

(5) Concentration by evaporation of the solution from which the iron has been removed.

(6) Evaporating further under closely controlled conditions the concentrated solution of aluminum chloride to selectively crystallize $AlCl_3 \cdot 6H_2O$, thereby separating the aluminum from dissolved minor constituent metals.

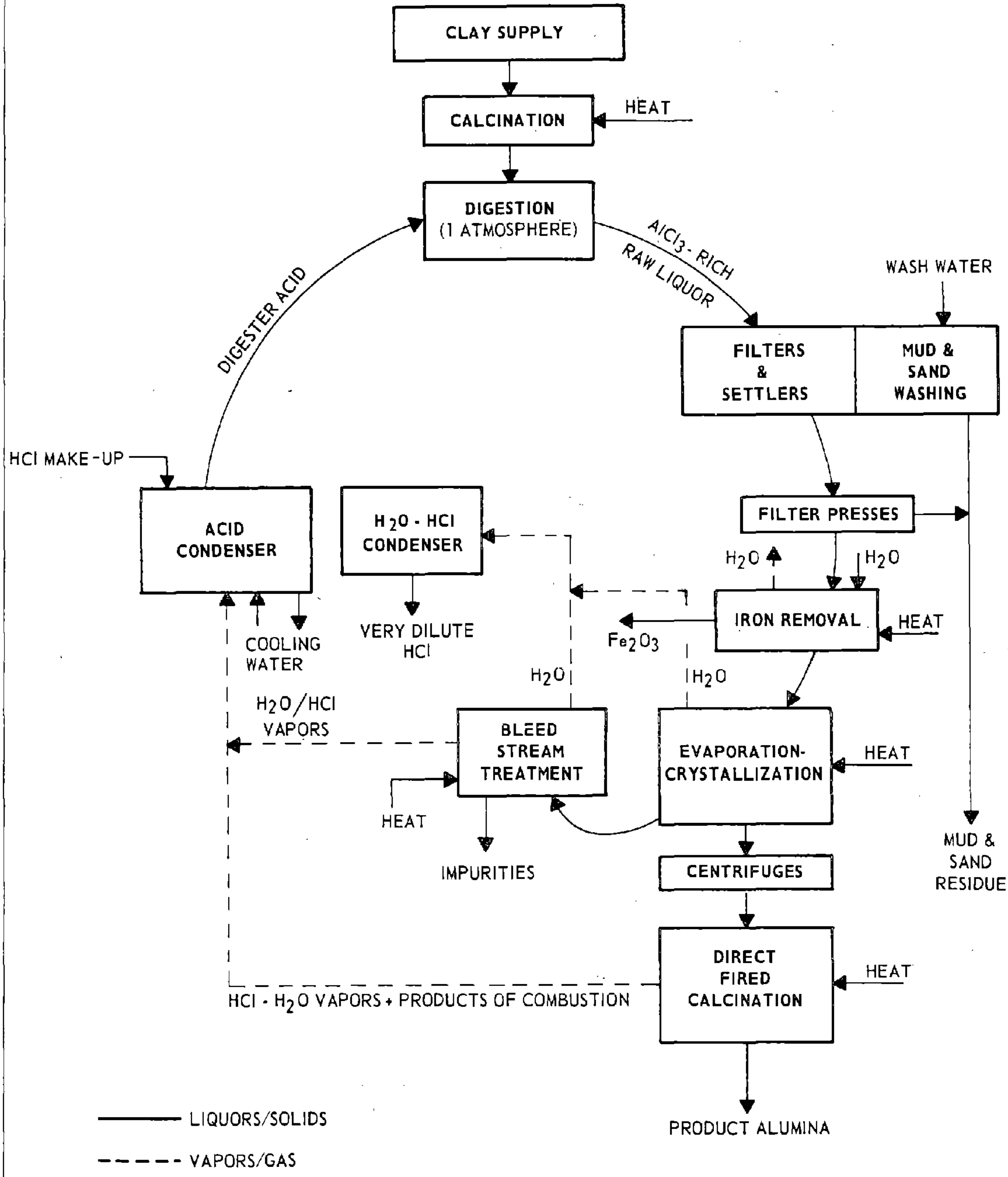
(7) Thermally decomposing the $AlCl_3 \cdot 6H_2O$ crystals to obtain the product alumina.

(8) Treating a fraction of the crystallizer mother liquor to reject soluble impurities remaining after crystallization, to recover hydrogen chloride, and to reject water. The soluble impurities, together with dissolved aluminum, are rejected as anhydrous waste solids.

(9) Recovering for recycle, by condensation and absorption, hydrochloric acid produced in thermal decomposition or elsewhere in the process.

FIGURE 4-2-1

ALUMINA FROM CLAY VIA HCL EXTRACTION
EVAPORATIVE CRYSTALLIZATION



(10) Conversion of iron chloride removed from the process to solid ferric oxide, with recovery of the contained chloride as hydrogen chloride.

The process being evaluated has been constructed from information derived from older U. S. Bureau of Mines reports of investigation, and the recent U. S. Bureau of Mines Report of Investigation No. 8188 describing a new solvent extraction process for iron removal, information published in the older open literature, and Kaiser Aluminum experience.

It is highly probable that alumina meeting reduction-grade chemical purity and physical property specifications can be manufactured from clay via hydrochloric acid extraction. The estimated net thermal energy requirement to process is 31.4 x 10^6 Btu/ton product alumina, which probably can be reduced somewhat by further studies and engineering design for heat recovery. All of the earlier studies of the thermal decomposition of $AlCl_3 \cdot 6H_2O$ were done with direct firing; if direct firing is used, a minimum of 14.5 x 10^6 Btu/ton alumina must be supplied by a clean fuel such as oil. Any fuel, including coal, may be used for the balance of the thermal energy requirement.

Hydrochloric acid losses can be held to low levels, and solutions for environmental problems are available.

Several process sections would benefit from the availability of additional engineering design information. These are clay calcination, solid-liquid separation, crystallization, product decomposition and bleed stream treatment for the removal of impurities.

4.2.2 Background

Interest in the use of hydrochloric acid as a means of extracting alumina from clay has existed since the turn of the century. Early investigators noted that:

(1) It was relatively easy to operate the leaching process so as to obtain almost quantitative separation of silica, and the silica was in a form which could be filtered and washed easily.

(2) Hydrochloric acid is an aggressive reagent which, after clay calcination, will dissolve up to 98% of the alumina in many U. S. kaolin clays with 2 hours leach time at the boiling temperature and at atmospheric pressure.

(3) The leaching process is exothermic, making it easy to reach and maintain the boiling temperature.

(4) Iron in the clay dissolves in about the same proportion as alumina. Titanium, sodium, potassium, calcium, and magnesium present in small amounts in accessory minerals tend to have much lesser, but variable, solubility in hydrochloric acid.

(5) High solution loadings of up to 200 g/l dissolved alumina are possible in the chloride system.

(6) Aluminum chloride hexahydrate can be crystallized from solution in a simple crystal of controlled particle size distribution. Only one hydrate forms, and the crystals are readily washed.

(7) Aluminum chloride hexahydrate decomposes without melting in its water of crystallization at comparatively low temperatures, although not completely excepting at higher temperatures.

(8) Hydrogen chloride is a very stable chemical compound. Chloride volatilized from aluminum chloride hexahydrate during thermal hydrolysis is completely converted into hydrogen chloride.

(9) Properties of the system $HCl-H_2O$ are well known, and properties of the systems M_xCl_y - HCl - H_2O for the metals of interest are known to a lesser but sufficient extent to allow the design of evaporators, crystallizers, acid recovery units, etc. Virtually complete recovery of HCl is possible if suitable conditions are chosen.

(10) The solubility of chlorides tends to increase with increasing temperature. Scaling problems on heat transfer surfaces are therefore eliminated or greatly reduced.

An important characteristic, recently discovered, is that virtually all of the metallic elements in the periodic system with the exceptions of sodium, potassium, calcium, magnesium, and aluminum form anionic chloride complexes. Iron, in particular, may be separated as an anionic chloride complex from the aluminum by solvent extraction using an appropriate organic extractant. Non-volatile organic extractants are available, which are almost insoluble in the aqueous phase, and which may be regenerated for reuse by stripping the iron chloride into a very dilute solution of hydrochloric acid. The iron-aluminum separation problem was a major barrier to the production of alumina from clay via hydrochloric acid extraction prior to development of the new solvent extraction technique.

The formation of anionic chloride complexes by most metals is probably at least partially responsible for the high separation factor achieved during crystallization. If the concentration of alkali and alkaline earth metals in the crystallizer are kept reasonably low by means of a bleed stream, $AlCl_3 \cdot 6H_2O$ crystals may be produced of sufficient purity as to be decomposable directly into reduction-grade alumina. It is fortunate that the amounts of these metal oxides present in many U. S. clays are very small in relation to alumina, and most of what is present may be in accessory minerals only partially soluble in hydrochloric acid.

The iron- aluminum separation mentioned above was instrumental in frustrating all previous efforts to use hydrochloric acid as a primary reagent in the extraction of alumina from clay. Materials of construction for tanks, piping, pumps, heat transfer surfaces, valves, and other equipment also presented a nearly insuperable problem before and during World War II, which was the last previous time of widespread interest in the extraction of alumina from clay. Fortunately, there have been major developments in corrosion resistant polymeric materials--both as linings and in solid form--since that time. Zirconium, titanium, tantalum or tantalum coatings, and resin impregnated graphite are available as corrosion resistant heat transfer surfaces in contact with acidic chloride solutions. A selection of metals protected by the development of oxide films may be used in the presence of HCl and H_2O above the dew point and under other specified conditions.

It is believed possible today to design a plant using hydrochloric acid as an extractant which will operate with an acceptable level of maintenance expense.

4.2.3 The Process

U. S. Bureau of Mines RI 6133 evaluates five hydrochloric acid processes for the extraction of alumina from clay, all of which have been rendered obsolete by the anionic chloride iron separation solvent extraction technology recently reported in USBM RI No. 8188. The process evaluated here has been constructed by Kaiser Aluminum primarily from information contained in RI 6133 and other technical literature cited in the bibliography which is a part of RI 6133, but taking advantage of the improved iron separation method of RI 8188. Azeotropic breaking distillation is employed in treating the crystallizer bleed stream. This latter process has been described in the U. S. patent literature and in Eastern European technical literature.

4.2.3.1 Summary

The entering clay is calcined for chemical activation, the removal of free and combined water, and the destruction of any organic materials. The calcined clay is leached with approximately 20% HCl at boiling and at atmospheric pressure, following which the insoluble solids are separated from the leach liquor and washed prior to their disposal. The combined leach liquor and washings are next subjected to solvent extraction for the removal of iron. One product of the solvent extraction-regeneration is a dilute acidic solution of ferric chloride. This solution is concentrated by evaporation and then thermally decomposed to ferric oxide, with recovery of its chloride content as hydrogen chloride.

The iron-free primary liquor is next subjected to multiple-effect vacuum evaporation to bring it to saturation with respect to aluminum chloride and then to further evaporation under controlled conditions to produce $AlCl_3 \cdot 6H_2O$ crystals of specified particle size distribution and purity. The crystals are separated from their mother liquor by vacuum filtration or low speed centrifuges, and adhering mother liquor is washed from them with 35% acid. The washed crystals are decomposed to product alumina by direct contact with hot combustion gases produced by burning a clean fuel. The combustion gases containing HCl and H_2O vapor produced by the thermal decomposition pass to a condenser-absorber where approximately 20% acid is recovered for recycle to leaching.

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The crystals recovered on the vacuum filter will carry with them adhering mother liquor. It is proposed to utilize this adhering mother liquor as the crystallizer bleed stream for the control of minor constituent impurity metals other than iron. The adhering liquor will be removed by the wash acid and delivered mixed with it to the HCl stripping column, where the used wash acid will be mixed with a much larger recirculating concentrated stream of waste chlorides. Hydrogen chloride is distilled off in concentrated form by an azeotropic-breaking distillation, most of the water in the entering wash acid remaining in the waste chloride solution. The hydrogen chloride vapor passes from the top of the stripper to an absorption column where it is absorbed into a side stream of recovered 20% acid to produce new 35% wash acid. The liquid from the bottom of the stripping column (which contains all of the metal chlorides, most of the water, and a small fraction of the hydrogen chloride in the entering wash liquid) passes into an evaporator for reconcentration. Steam containing some hydrogen chloride passes into the primary acid recovery unit. Most of the reconcentrated waste chloride stream is recycled to the HCl stripper, but the net production is sent to waste solids decomposition. Sulfuric acid equivalent to calcium, magnesium, sodium, and potassium is added in this latter unit, which is a calciner. Waste solids are discharged, and hydrogen chloride recovered is sent to the HCl absorber.

4.2.3.2 Calcination

Entering clay is calcined in the same manner as for processes employing nitric or sulfurous acids as the aluminum extractant. All of the comments made in the evaluations of the processes employing those acids as extractants--and in particular to the possible development of fluidized solids clay calcination--apply equally when employing hydrochloric acid as the extractant.

4.2.3.3 Leaching

Alumina dissolves during leaching

$$\underset{\text{Calcined clay}}{Al_2O_3 \cdot 2SiO_2} + \underset{\text{Solution}}{6HCl} \longrightarrow \underset{\text{Solution}}{2AlCl_3} + 3H_2O + \underset{\text{Solid Waste}}{2SiO_2}$$

The tanks employed for leaching may be constructed of mild steel with a polymeric lining, protected against abrasion and excessive temperature by an inner brick lining. Free-standing fiberglass-reinforced plastic (FRP) tanks, also protected by a brick lining, are a possible alternative. The tanks will have sealing covers so that vapors generated by the heat of reaction may be contained and conducted to a condenser. Gentle agitation will meet the objectives of assuring adequate access of acid to all of the solid particles while avoiding, insofar as practical, attrition of the clay particles during leaching. It is further expected that the leaching will be accomplished cocurrently in three to five stages at one atmosphere at the boiling temperature with solution extraction of 90-98% of the total entering aluminum within a total residence time of about 2 hours.

Adequate information is available today for the design of a leaching operation that will operate successfully. Some additional study is desirable to develop a design which will minimize feed particle attrition. This is important in minimizing the production of fines, which would make the subsequent solid-liquid separation and residue washing step more difficult and costly.

4.2.3.4 Solid-Liquid Separation

The amount of waste solids is large enough to require, under optimum conditions, a substantial capital investment in the separation, washing, and solids handling operations and to require the introduction of a substantial amount of waste solids wash water into the process. This wash water must later be removed by evaporation in order to maintain the process water balance.

Enough is known about the properties of the residue and solution produced by hydrochloric acid leaching of U. S. kaolin clay to make possible the engineering design of a solid-liquid separation system which would operate. Much work however remains to be done on optimizing the solid-liquid separation in terms of the capital cost for the operation and the dilution water introduced. This must, as in the case of nitric acid leaching, be done in conjunction with design of the leaching operation, because the characteristics of the solids emerging from leaching will control the solid-liquid separation.

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4.2.3.5 Iron Removal

The removal of iron at this point is desirable to insure that it does not enter crystallization, thereby insuring its exclusion from the final product. Removal of iron prior to evaporation also makes it possible to enter crystallization with a pregnant liquor containing a higher concentration of dissolved alumina.

The first step in iron removal is quantitative oxidation of the iron to the ferric state in order to render it amenable to solvent extraction. It is recommended that this be accomplished by means of elemental chlorine, which oxidizes ferrous iron very quickly according to the reaction

$$Fe^{++} + \tfrac{1}{2}Cl_2 \longrightarrow Fe^{+++} + Cl^-$$

The oxidation process can be readily monitored and an excess of chlorine avoided through the well-developed use of an oxidation potential measurement. A further advantage of chlorine as an oxidant is that it is converted to chloride which supplies part of the over-all process chloride makeup requirement.

Enough is known about chlorine oxidation to embody it in a demonstration plant design without further development work.

The U. S. Bureau of Mines in RI 8188 has described an excellent separation of iron from aluminum which comprises a multistage countercurrent solvent extraction of ferric iron into a mixture of certain amine hydrochlorides dissolved in an organic solvent.

The reaction for formation of the anionic chloride complex is:

$$FeCl_3 + Cl^- \longrightarrow FeCl_4^-$$

and for the extraction is:

$$\underset{\text{aqueous}}{FeCl_4^-} + \underset{\text{organic}}{R'RNH^+Cl^-} \longrightarrow \underset{\text{organic}}{R'RNH^+FeCl_4^-} + \underset{\text{aqueous}}{Cl^-}$$

The equipment used was mixer-settlers. The organic was regenerated for recycling in a similar multistage operation by stripping it into water containing just enough hydrochloric acid to avoid precipitating basic ferric compounds.

The equation for the stripping step is:

$$\underset{\text{organic}}{R'RNH^+FeCl_4^-} + \text{water} \longrightarrow \underset{\text{organic}}{R'RNH^+Cl^-} + \underset{\text{aqueous}}{FeCl_3}$$

Enough information has been developed about this operation to permit design of a demonstration plant without further development work.

The strip solution produced during regeneration of the organic extractant is acidic and contains approximately 3.5% ferric chloride. This solution is concentrated by multiple effect evaporation to approximately 50% ferric chloride, at which concentration it is sprayed onto particles of iron oxide in a direct-fired fluid bed at a temperature of approximately 1500°F. The ferric chloride immediately decomposes:

$$\underset{\text{solution}}{2FeCl_3 + (n+3)H_2O} \xrightarrow{\Delta H} \underset{\text{solid}}{Fe_2O_3} + \underset{\text{(vapor)}}{6HCl\uparrow} + \underset{\text{(vapor)}}{nH_2O\uparrow}$$

The vapors plus inerts and combustion products pass to acid recovery. The iron oxide goes to waste disposal, or it may be sold as iron ore.

The technology of iron chloride decomposition has been previously well developed in connection with the treatment of steel mill pickle liquors. It is expected that no additional development effort will be required.

4.2.3.6 Evaporation

Concentration of the iron-free pregnant liquor to saturation brings the liquor to the point where crystallization of $AlCl_3 \cdot 6H_2O$ may begin. It also provides a means of rejecting water, thus helping to maintain the over-all process water balance.

Approximately 9.6 mass units of water/unit product alumina, along with all of the free dissolved HCl, are removed by evaporation from the iron-free leach liquor (including diluted leach liquor

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recovered by washing the waste solids) to produce a 31% solution of aluminum chloride.

Acid vapors produced during evaporation may be totally condensed or may be condensed stagewise to obtain a liquid acid the concentration of which will depend upon the ratio $HCl:H_2O$ in the vapor entering the condenser and the pressure (temperature) at which the condenser is operating. Under the circumstances existing during concentration of the pregnant liquor, it will be possible by stagewise condensation to recover all of the hydrogen chloride in the vapor as liquid acid of at least 10% HCl and to recover the remainder as water.

This evaporation may be done under vacuum in order to utilize heat recoverable in other sections of the process. The technology of the evaporative process is well known and should require very little additional development work.

4.2.3.7 Crystallization

Cooling crystallization is not effective for producing $AlCl_3 \cdot 6H_2O$ because the solubility of aluminum chloride decreases only slightly as the temperature is decreased. The saturated solution from the evaporators is therefore continuously passed into evaporative crystallizers where all of the water in which the aluminum chloride is dissolved (in excess of that required for the formation of $AlCl_3 \cdot 6H_2O$) is evaporated under controlled conditions. This induces supersaturation, with the consequent formation of crystals.

Heat is absorbed when $AlCl_3 \cdot 6H_2O$ crystals form. This crystallization process requires a substantial amount of heat because heat must be supplied both for evaporation of the water and for formation of the crystals.

Ideally, only water vapor and $AlCl_3 \cdot 6H_2O$ crystals would leave the crystallizer. In practice a mother liquor bleed stream must also be taken out in order to control the buildup of soluble impurities entering the crystallizer. It is possible that mother liquor adhering to the crystals as they are recovered, as discussed in the next section, may provide the required amount of bleed. The technology of the crystallization step is well known, and no additional development work is required prior to designing a demonstration plant.

4.2.3.8 Crystal Recovery

The $AlCl_3 \cdot 6H_2O$ crystals may be separated from the crystallizer mother liquor by either vacuum filtration or centrifuges. Some mother liquor will inevitably adhere to the crystals; this mother liquor can probably provide the bleed stream required for control of minor constituent impurities in the crystallizer. The crystals are therefore washed with 35% hydrochloric acid, in which aluminum chloride has a very low solubility, to free them of adhering mother liquor.

Design of the crystal recovery and acid washing section of a demonstration plant is not expected to require any substantial amount of further development work.

4.2.3.9 Decomposition

The crystals next pass to thermal decomposition. $AlCl_3 \cdot 6H_2O$ crystals decompose very rapidly when heated to temperatures above about 375°F approximately in accordance with the reaction

$$2AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 9H_2O\uparrow$$

but the decomposition does not proceed within a reasonable time to a composition of residual chloride of 0.1% unless a final calcination temperature of approximately 1650°F is attained. The presence of a high partial pressure of steam facilitates removal of the chloride. It appears that alumina can be produced which will meet or exceed all specifications for chemical purity with the possible exception of the present target specification for residual chloride. It also appears possible that alumina can be produced which will have a suitable surface area, which will dissolve readily in the reduction cell cryolite bath, and which will have an acceptable particle size distribution.

The thermal decomposition process is energy intensive, requiring approximately 14.5×10^6 Btu/ton product alumina if it is assumed that the alumina leaves decomposition at 1300°F and that the gaseous products exit at 600°F. No provision is included in the above requirement for steam that may be supplied in the final stage(s) of decomposition. The required thermal energy may be supplied by direct contact of the crystals with hot combustion products; but if this option is chosen, a clean fuel is required. If indirect heating is selected, a suitable heat transfer medium and heat transfer surface material of construction must be chosen.

The published literature describes the employment of Herreschoff-type furnaces and rotary kilns, both directly and indirectly fired, for accomplishing the decomposition. Further development of equipment for carrying out the thermal decomposition operation, even if a direct-fired decomposition employing a clean fuel is chosen, is required before an economically competitive demonstration plant can be designed. This process evaluation is based upon the employment of direct-fired decomposition.

4.2.3.10 Acid Recovery

The recovery of hydrochloric acid from hot vapors is simpler than for nitrogen or sulfur-based acids, because no decomposition of hydrogen chloride occurs at any process temperature and because of the great affinity of hydrogen chloride for water.

The equilibrium partial pressure of HCl over water containing small percentages of HCl is extremely low even at the normal boiling temperature of such solutions, and the volatility of HCl in relation to water decreases with decreasing temperature. An azeotrope exists at one atmosphere in HCl/H_2O solutions at 20.2% HCl.

The above properties determine the conditions of operation which are possible for the acid recovery system. The three important factors in the recovery of hydrochloric acid from condensing vapors are the ratio $HCl:H_2O$, the temperature at which the system is operating, and the amount of inert gases which are present. Virtually complete recovery of HCl is possible from the gases exiting a direct-fired thermal decomposition of $AlCl_3 \cdot 6H_2O$. A countercurrent flow condenser may be used to condense the decomposer off-gases and produce approximately 20% HCl while rejecting H_2O vapor and inert gases.

Equipment for recovering hydrochloric acid from the vapors produced by a direct-fired thermal decomposition operation at demonstration plant scale can be designed without further development.

4.2.3.11 Bleed Stream Treatment

Mother liquor adhering to the $AlCl_3 \cdot 6H_2O$ crystals, withdrawal of which also serves the purpose of removing soluble minor constituent impurities from the process is recovered after washing of the crystals in admixture with the wash acid. Further treatment of these very acidic washings has three functions:

(1) rejection of the impurities in the liquor washed from the crystals;

(2) recovery as fresh concentrated wash acid of the HCl contained in the washings;

(3) rejection of water from the process.

The washings are mixed in a stripping column with a hot, concentrated, recycling stream of previously separated waste alkali and alkaline earth metal chlorides so as to prepare after mixing, on an HCl-free basis, a solution approximately 40% H_2O and 60% waste chlorides. The presence of the high metal chloride concentration is known to greatly increase the volatility of the HCl in relation to H_2O, the latter having a great affinity for the dissolved $MgCl_2$ and $CaCl_2$. Almost pure HCl vapor exits the top of the column, whereas the bottom liquid contains only a small amount of HCl but nearly all of the H_2O in the washings being processed.

Concentrated HCl vapor from the top of the column passes into an absorption column where it increases the concentration of a sidestream of acid from the primary absorber from 20-22% to 35%. This becomes fresh wash acid. The somewhat diluted waste chloride stream passes to an evaporator where it is reconcentrated. The major fraction of the reconcentrated waste chloride stream is recycled to stripping, but the net production is withdrawn for further treatment described below. Acidic vapors proceed to the primary acid condenser for recovery of contained HCl, the associated water vapor being rejected to the stack.

The chemical engineering principles involved in the addition of a third component to a two-component system in order to make possible separation of the original two components by distillation is well known. There is reportedly one commercial installation

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in the U. S. of this method for separating HCl and H_2O. Other commercial installations have been reported in Eastern Europe, and a partially analogous operation has been reported in Israel. There appears to be very little doubt that the method is operable, but piloting is recommended prior to design of a demonstration plant to solve problems that may arise due to the presence of aluminum chloride, the possible formation of double salts, etc. The pilot study should be based upon a recirculating waste chloride solution of a composition that would be derived from a particular clay.

4.2.3.12 Sulfuric Acid Treatment of Waste Chlorides

The net production of concentrated waste chlorides is treated with sulfuric acid equivalent to the alkali and alkaline earth metals present (but not equivalent to alumina) and calcined. Representative reactions occurring are:

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl\uparrow$$

$$2AlCl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl\uparrow$$

The HCl produced is relatively concentrated and is sent to concentrated acid absorption. The mixture of sulfates and alumina is waste.

The technology of the calcination of chlorides with sulfuric acid to produce metal sulfates plus HCl is well known. No further development work is necessary prior to design of a demonstration plant.

4.2.4 Energy Requirements

The net energy requirements to process for HCl extraction-evaporative crystallization are:

	Btu/ton Al_2O_3
Clay calcination	5.5×10^6
Iron removal	1.7×10^6
Evaporation plus Crystallization	8.4×10^6
Thermal decomposition	14.5×10^6
Bleed stream treatment	1.3×10^6
	31.4×10^6

It is important that the direct-fired thermal decomposition of $AlCl_3 \cdot 6H_2O$, although technically simpler than an indirect-fired decomposition because it avoids the need for heat transfer surfaces and media, will require a clean fuel which probably will be oil. This will be costly in view of the large heat requirement for this process section.

Waste heat may be recovered from the condensation of hydrochloric acid by innovative design in the acid recovery section. This heat could be employed in vacuum evaporation to reduce the amount of steam otherwise required.

Steam requirements can be met by coal-fired boilers.

4.2.5 Environmental Control

It will be necessary to construct as a closed system with respect to the environment those plant sections where hydrogen chloride is present in order to safeguard the health of the workmen, avoid excessive maintenance costs, avoid acid losses, and meet anticipated emission standards. Fortunately, this task is made easier by the great affinity of hydrogen chloride for water. Covered leach tanks, for example, can be vented to the atmosphere through a condenser. Filters must be covered but also can be vented to the atmosphere through a condenser/scrubber.

Recovery of hydrogen chloride to meet air pollution control requirements can be assured in the acid recovery section.

Waste solids from leaching will comprise silica, a small amount of unreacted clay, and small amounts of unreacted accessory minerals. The silica will not be excessively hydrated, and these waste solids should make a good subsoil. It will undoubtedly be desirable to return them to mined-out areas for disposal, but small amounts of chloride remaining in them--which may accidentally find its way into the groundwater--will be indistinguishable from chlorides which are natural constituents of groundwaters. Other waste solids from the process are iron oxide and a mixture of metal sulfates with alumina. The iron oxide may be disposed of with the leach solids or may have some value. The sulfate-alumina mixture will require disposal in a manner such that the sulfates will not be leached out or where the presence of dissolved sulfate will not be objectionable. The quantity of sulfates produced in relation to alumina will be small.

Heat entering the process is largely rejected to the atmosphere in combustion gas streams or by means of cooling towers. The process does not produce a liquid effluent other than the water present in the waste leach solids. Current technology permits return of this water to the process.

4.2.6 Alumina Product Quality

Experimental evidence based upon literature, some direct laboratory work, and some miniplant results all indicate that the chemical purity of chloride process alumina with respect to metals has the potential of being considerably higher than Bayer process aluminas. The extent to which chloride may be economically removed from such aluminas, and the actual extent to which reduction plant operations will require its removal, are not known with certainty at this time. Phosphate is a material present only in trace quantities in the entering clay. It is not expected to cause difficulty in the hydrochloric acid extraction of alumina from clay, but the P_2O_5 specification in the finished alumina is very low; and very little is known about the passage of phosphate through the processing cycle.

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Tests on small quantities of chloride process alumina have shown that it can be produced to meet present day specifications for surface area and water absorption. This alumina also appears to dissolve very readily in molten cryolite. It will be possible to produce $AlCl_3 \cdot 6H_2O$ crystals in a particle size distribution appropriate as the precursor to the finished alumina. Assuming that a decomposition process can be developed which--in addition to meeting other requirements--will minimize attrition, it is probable that the particle size distribution specification can also be met. The finished alumina will be less dense than Bayer alumina, but chloride process alumina can be produced with a constant density.

4.2.7 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000 ton/d of alumina.

(2) The chemical analysis of the clay feed (dry basis) is as follows:

Al_2O_3	36.5%
Fe_2O_3	0.86
SiO_2	46.4
L. O. I.	13.54
Other*	2.7
	100.00%

*Other is primarily TiO_2.

(3) The raw clay feed to the process contains 18.5% free moisture.

(4) A rotary kiln is used for the calcination of the clay feedstock.

(5) There is a 1% dust loss (calcined basis) from the rotary kilns used to calcine the raw clay.

(6) 20% by weight hydrochloric acid is utilized as leach acid.

(7) 15% of the heat of reaction in the leaching tanks is released in the form of vapors. These vapors contain 1% HCl and are condensed and returned to the leach tanks.

(8) 95% extraction efficiency of Al_2O_3 is achieved in the leaching step.

(9) 95% of Fe_2O_3 is solubilized in the leaching step.

(10) 7.2% of "other" (approximately the same as in the HNO_3 process) is solubilized in the leaching step. This soluble fraction mainly consists of sodium, potassium, calcium, and magnesium salts plus phosphate and sulfate.

(11) Approximately 10% excess HCl is contained in the leach acid.

(12) The underflow from the settling and washing units contains 33% solids by weight.

(13) Filter press solids from pregnant liquor polish filtration contains 60% solids.

(14) 1% of the soluble alumina is lost in the leach waste residues.

(15) Chlorine is added to the pregnant liquor before solvent exraction based upon one third of soluble iron content being present as ferrous iron.

(16) 100% of the chlorine added is converted to HCl.

(17) A solution of 10% Alamine 336 in kerosene is used as the organic extractant for ferric iron.

(18) The iron content in the pregnant solution from solvent extraction is reduced to about 0.001 grams per liter.

(19) A volume ratio of aqueous/organic of 3/1 is present during extraction.

(20) A volume ratio of organic/aqueous of 3.5/1 is present during stripping.

(21) The strip acid will contain approximately .03% HCl.

(22) The recycled organic solution to extraction will contain about 0.5 grams per liter Fe.

(23) The organic loss is taken as 2.1 lb per ton Al_2O_3 or 1 ton/d.

(24) Use of the distribution coefficient of .004 for aluminum when using Alamine 336 is equivalent to a loss of 10 ton/d of $AlCl_3$ in the solvent extraction section.

(25) Multiple effect evaporators (3-effect) and evaporative crystallizers are used for the concentration and crystallization of $AlCl_3 \cdot 6H_2O$ intermediate product.

(26) The slurry from the $AlCl_3$ crystallizers contains 30% solids by weight and a residual 13.6% $AlCl_3$ in solution.

(27) The $AlCl_3 \cdot 6H_2O$ crystal slurry from the crystallizer is filtered and washed on vacuum filters yielding a cake containing 85% solids.

(28) Filtrate mother liquor is recycled to the crystallizer.

(29) The bleed stream for minor impurities purging ("other") is the washings filtrate from vacuum filtration.

(30) One displacement wash of 35% HCl at an 83% washing efficiency is used on the product $AlCl_3 \cdot 6H_2O$ crystals.

(31) The washed $AlCl_3 \cdot 6H_2O$ crystals are decomposed in direct fired rotary kilns.

(32) There is a 1% dust loss (calcined basis) from the decomposition and calcination of $AlCl_3 \cdot 6H_2O$ crystals.

(33) The product alumina will contain 0.01% residual Cl_2.

(34) Only combustion water has been included in the material balance of direct-fired heating units.

(35) 1% of the HCl and H_2O from the product decomposition is lost in the subsequent acid recovery operation.

(36) The washings filtrate bleed is stripped to remove 93% of free HCl and evaporated in multiple effect evaporators to a 45% solution of chlorides.

(37) Sufficient liquor from the evaporator is recycled to maintain a 40% solution of chlorides in the HCl stripping step.

(38) A stoichiometric quantity of H_2SO_4 for "other" is added before the waste chlorides decomposition.

(39) The stripping solution is concentrated to a 50% solution of chlorides in a multiple effect evaporator before decomposition in a direct fired fluid bed decomposer.

(40) Makeup HCl is added as a 35% acid wash to the $AlCl_3 \cdot 6H_2O$ vacuum filter.

(41) A 53°F temperature rise occurs in cooling water.

(42) Theoretical heat requirements divided by .85 to estimate actual heat requirements. This method used only when no actual data was available.

TABLE 4-2-1

ALUMINA FROM CLAY HYDROCHLORIC ACID PROCESS/EVAPORATIVE CRYSTALLIZATION DAILY THERMAL REQUIREMENTS FOR 1,000 TON/D Al_2O_3

	100 LB/IN^2 (GA) STEAM, M LBS (881 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
CLAY PREPARATION			
CALCINATION	–	5,507	–
LEACHING			
LEACHING CONDENSER	–	–	449
EVAPORATION			
EVAPORATION & CRYSTALLIZING (3-EFFECT)	9,567	–	8,955
DECOMPOSITION & CALCINATION			
ROTARY KILN	–	14,500	–
BLEED STREAM PROCESSING			
HCl STRIPPING	367	–	–
EVAPORATION (3-EFFECT)	547	–	–
DECOMPOSITION	–	500	–
STRIPPING SOLUTION PROCESSING			
EVAPORATION (3-EFFECT)	1,449	–	–
DECOMPOSITION	–	400	–
ACID RECOVERY			
HCl ABSORPTION	–	–	1,575
HCl CONDENSER	–	–	23,478
TOTALS	**11,930** **(10,510 MM BTU)**	**20,907**	**34,457**

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 31,417 MM BTU/D *OR* 31.4 MM BTU/TON Al_2O_3

Table 4-2-2 (Sheet 1 of 6)

Alumina from Clay/Hydrochloric Acid Process
Evaporative Crystallization
Material Balance

1,000 TON/D Al_2O_3

Process Stream	1	2	3	4	5	6	7	8	9	10	11
Component											
Al_2O_3	1127	1127	1116	1116			56	56		56	
$AlCl_3$							2776	557		27	530
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3	27	27	27	27			1	1		1	
$FeCl_3$							52	11			11
HCl					2	2	229	46	1	1	46
L.O.I.	418	418									
H_2O	701	701			198	198	10734	2491	4719	3147	4063
Other	84	84	83	83			83	78		77	1
SiO_2	1433	1433	1419	1419			1419	1419		1411	8
Organic											
H_2SO_4											
Cl_2											
Total	3790	3790	2645	2645	200	200	15350	4659	4720	4720	4659

All units are in short tons per day.

Table 4-2-2 (Sheet 2 of 6)

Alumina from Clay/Hydrochloric Acid Process
Evaporative Crystallization
Material Balance

Process Stream	12	13	14	15	16	17	18	19	20	21	22
Component											
Al_2O_3											
$AlCl_3$	2749		1	2748		2738	2738	1506	1392	20	
$AlCl_3 \cdot 6H_2O$								4746		4746	
Fe_2O_3											
$FeCl_3$	52			52							
HCl	229			229		240	149	1971	1822	268	
L.O.I.											
H_2O	12306	6	6	12306		12306	2691	7523	6954	549	983
Other	6			6		6	6	74	68	1	
SiO_2	8		8								
Organic											
H_2SO_4											
Cl_2					11						
Total	15350	6	15	15341	11	15290	5584	15820	10236	5584	983

Table 4-2-2 (Sheet 3 of 6)

Alumina from Clay/Hydrochloric Acid Process
Evaporative Crystallization
Material Balance

Process Stream	23	24	25	26	27	28	29	30	31	32	33
Component											
Al_2O_3	1000	10									
$AlCl_3$								94			
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3											
$FeCl_3$											
HCl	1		2435		24	2467	39	174	157	254	
L.O.I.											
H_2O			3120	2089	31	9868	73	565	3	472	281
Other	1							5			
SiO_2											
Organic					1						
H_2SO_4											
Cl_2											
Total	1002	10	5555	2089	56	2335	112	838	160	726	281

Table 4-2-2 (Sheet 4 of 6)

Alumina from Clay/Hydrochloric Acid Process
Evaporative Crystallization
Material Balance

Process Stream	34	35	36	37	38	39	40	41	42	43	44
Component											
Al_2O_3											
$AlCl_3$										1435	1341
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3											
$FeCl_3$											
HCl	15		1	2	2	91	89	74	2541	88	71
L.O.I.											
H_2O	60	4189	64	9259	9259	9615	356	296	10164	2374	1812
Other										76	71
SiO_2											
Organic											
H_2SO_4											
Cl_2											
Total	75	4189	65	9261	9261	9706	445	370	12705	3973	3295

Table 4-2-2 (Sheet 5 of 6)

Alumina from Clay/Hydrochloric Acid Process
Evaporative Crystallization
Material Balance

Process Stream	45	46	47	48	49	50	51	52	53	54	55
Component											
Al_2O_3						36					
$AlCl_3$		94					10			10	
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3											
$FeCl_3$							59	7		52	
HCl	12	5			82					1	
L.O.I.											
H_2O	435	127		20	128					1249	1185
Other		5				12					
SiO_2											
Organic							3781	3780	1	1	
H_2SO_4			7								
Cl_2											
Total	447	231	7	20	210	48	3850	3787	1	1313	1185

Table 4-2-2 (Sheet 6 of 6)

Alumina from Clay/Hydrochloric Acid Process Evaporative Crystallization Material Balance

Process Stream	56	57	58	59	60	61					
Component											
Al_2O_3				4	11						
$AlCl_3$		10									
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3				26							
$FeCl_3$		52									
HCl	1	1				44					
L.O.I.					418						
H_2O	1249	64	13		701	66					
Other					1						
SiO_2					14						
Organic		1				1					
H_2SO_4											
Cl_2											
Total	1250	128	13	30	1145	111					

4.2.8 Equipment List

ALUMINA FROM HYDROCHLORIC ACID/CLAY EVAPORATIVE CRYSTALLIZATION PROCESS

Clay Preparation Area

Belt conveyor under wobbler feeder and primary crusher
Truck dump hopper
Wobbler feeder and hoppers from truck dump
Primary crusher and chutes
Belt conveyor: primary crushers to stockpile
Belt conveyor and distributors for stockpile
Stockpile, enclosure, dust collection system and reclaim system
Wobbler feeder from stockpile
Belt conveyor, stockpile to hammermills
Hammermills and hoppers
Belt conveyor, hammermills to elevator
Bucket elevators from secondary crusher
Vibrating screens, chutes and covers
Roll compactors with covers
Belt conveyor compactors to elevators
Belt conveyor screens to raw clay surge bin
Raw clay surge bin
Weigh belt feeders
Belt conveyors raw clay surge bin to kilns
Rotary kilns
Apron feeders with covers from coolers
Calcine bucket elevators
Calcine vibrating screens and chutes
Calcine cage mill grinder with covers
Calcine apron feeder with cover
Bucket elevator to calcine storage bins
Calcine storage bins
Weigh belt feeders to leaching
Belt conveyors to leach tanks
Dust collection system

Leaching, Thickening, CCD Washing and Filtration Area

Leach tank screw feeders
Leach tanks (lined)

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EQUIPMENT LIST (Cont)

Leach tank agitators
Leach tank recirculating pumps
Leach tank vapor condensers
Leach flash tanks
Leach slurry pumps
Flash vapor condensers
Leaching condensate tanks and ejectors
Leaching condensate pumps
Dilute HCl transfer pumps
Sand thickener tanks
Sand thickener rakes
Sand thickener underflow pumps
Sand thickener overflow pumps
Sand washer tanks
Sand washer rakes
Sand washer underflow pumps
Sand washer overflow pumps
Sand slurry tank (lined)
Sand slurry pumps
Flocculant prep system (HNO_3)

Filter presses
Vibrating screens
Press cake relay tanks
Filtrate tanks
Filtrate pumps
Repulped slurry pumps
In-line chlorine blender
Collecting sluice
Spent filter and dumpers
Filter aid storage tank
Filter aid conveyor and weigh feeder
Filter aid slurry tanks
Filter aid slurry tank agitators
Filter aid slurry pumps
Filter aid liquor pumps

Fe Removal, Stripping, $FeCl_3$ Evaporation Decomposition Area

Solvent surge tank (lined)
Solvent surge tank pumps

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EQUIPMENT LIST (Cont)

Head tanks
Mixer settlers
Mixer settler covers
Loaded solvent pumps
Mixing pumps and baffles
Raffinate pumps
Raffinate storage tank (lined)
Raffinate storage pumps
Loaded solvent surge tank (lined)
Loaded solvent surge tank pumps
Regenerated solvent pumps
Wash water tank
Wash water tank pumps
Spent $FeCl_3$ pumps
$FeCl_3$ solution tanks
$FeCl_3$ solution tank pumps
Decanol unloading pump
Kerosene unloading pump
Alamine unloading pump
Decanol storage tank
Kerosene storage tank
Alamine storage tank
Decanol blending pumps
Kerosene blending pumps
Alamine blending pumps
Solvent blend tank
Solvent make-up pumps
$FeCl_3$ multiple-effect evaporator system
$FeCl_3$ evaporator condensers
$FeCl_3$ decomposer system

Evaporation, Crystallization, Centrifuging Area

Pregnant liquor evaporation system
$AlCl_3 \cdot 6H_2O$ crystallizer system
1st stage crystallizer product centrifuges
2nd stage crystallizer product centrifuges
1st stage centrate tanks
2nd stage centrate tanks
Hydroclones

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EQUIPMENT LIST (Cont)

1st stage centrifuge wash tanks
2nd stage centrifuge wash tanks
Centrifuge wash pumps
1st stage centrate pumps
2nd stage centrate pumps
$AlCl_3 \cdot 6H_2O$ crystal bins
Weigh feeders
1st stage centrifuge conveyors
2nd stage centrifuge conveyors
Crystals conveyors to decomposition
HCl storage tanks
HCl transfer pumps
HCl fumes absorbers
Centrifuge discharge conveyors

$AlCl_3 \cdot 6H_2O$ Decomposition Area

$AlCl_3 \cdot 6H_2O$ decomposition system (including feed hoppers, screw conveyors, 3-stage fluidized bed decomposers and fluid bed coolers)

HCl Condensing, Stripping, Absorption Area

Hydrogen chloride condensers (lined and packed)
Condenser underflow pumps
Condenser recirculation cooler
Stripper (lined and packed)
Stripper reboiler
Stripper underflow pumps
Stripper product pumps
HCl quench tower
Falling film absorber
Tails tower (lined and packed)
Absorber underflow pumps
Product cooler

HCl Vapor Condensing Area

Evaporator condensers
Crystallizer condensers

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EQUIPMENT LIST (Cont)

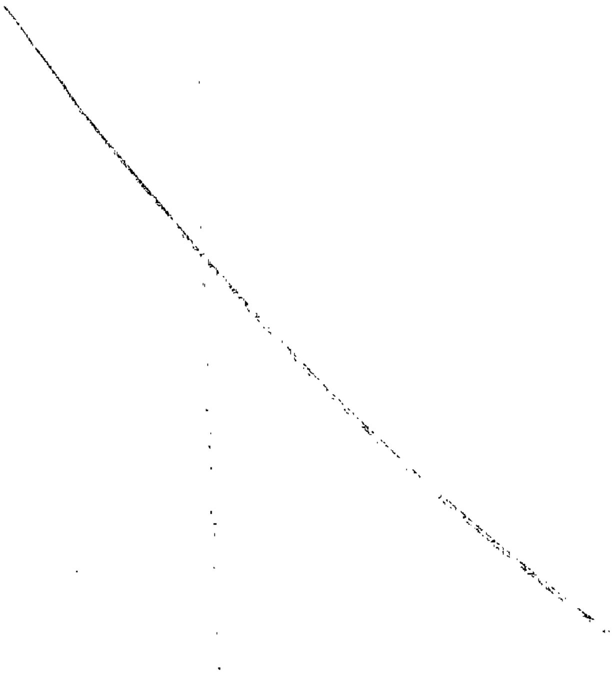
Evaporator condenser condensate pumps
Crystallizer condenser condensate pumps
Steam ejectors
Ejector sump (lined)
Ejector sump pumps
Accumulator tank
Accumulator pumps
Accumulator cooler

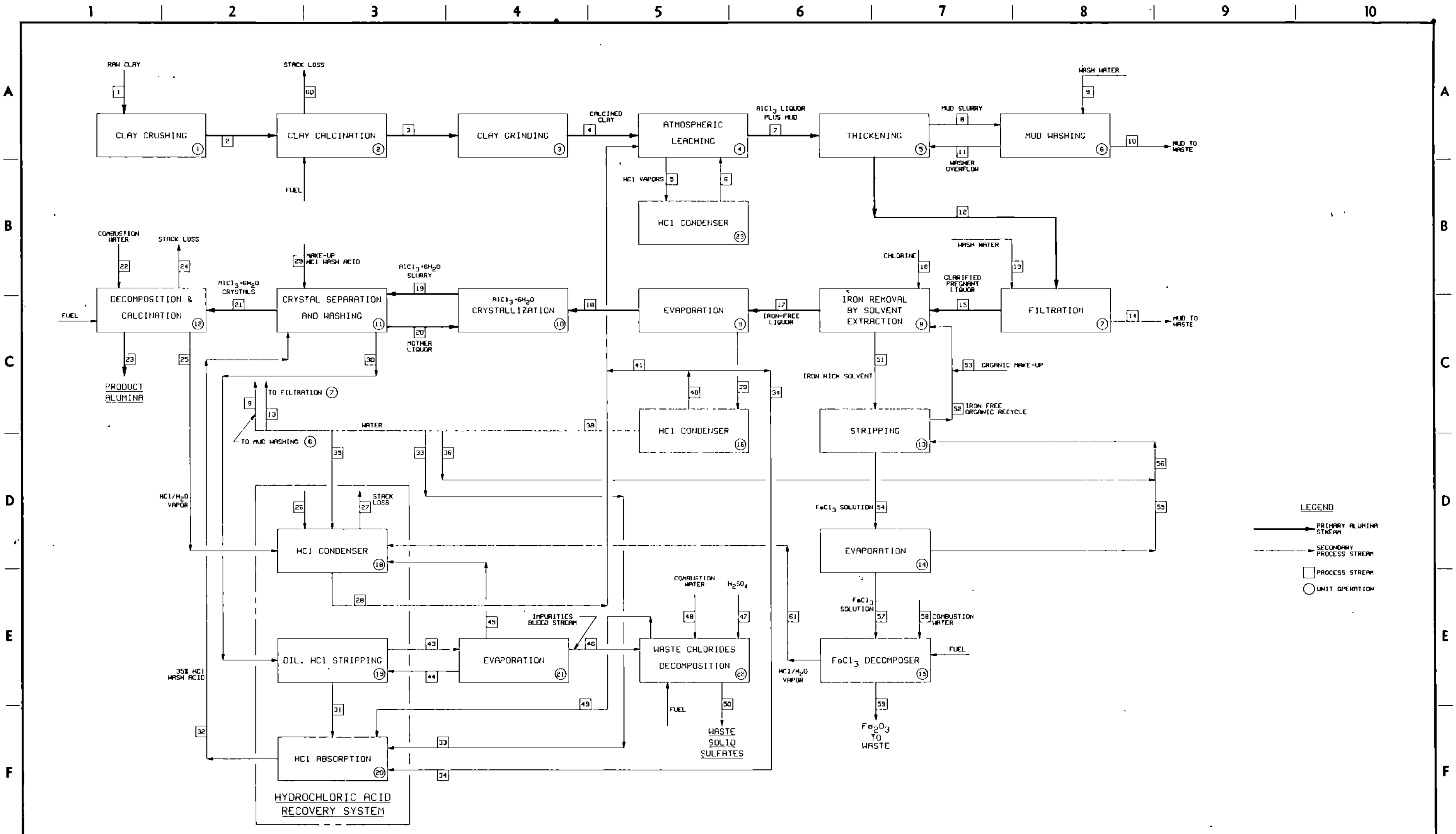
Waste Chlorides Evaporation and Decomposition Area

Evaporator
Separator (lined)
Waste chloride decomposer

Utilities

Steam plant and auxiliary systems
Cooling towers and auxiliary systems





NO.	DATE	REVISION	BY	APP	APP

NOTES

FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-2-2

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-2-1

DESCRIPTION COST ACCOUNT

WORK COVERED BY THIS DRAWING CHARGED TO COST ACCOUNT ABOVE

CONSTRUCTION APPROVAL

APPROVAL	DATE	SCALE	DATE
		DESIGNED BY	
		DRAWN BY ADS	
		CHECKED BY	
		APPROVED BY	
		APPROVED BY	

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO. J0265048

ALUMINA FROM CLAY
HYDROCHLORIC ACID PROCESS
EVAPORATIVE CRYSTALLIZATION

JOB No. 76161-001 FIGURE NO. 4-2-2 REVISION R-0

NOT REPRODUCIBLE

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4.3 TECHNICAL APPRAISAL: ALUMINA FROM CLAY VIA HYDROCHLORIC ACID EXTRACTION - HCl GAS-INDUCED CRYSTALLIZATION

4.3.1 Summary and Conclusions

The process being evaluated for the manufacture of reduction-grade alumina from clay via hydrochloric acid extraction with HCl-induced crystallization of $AlCl_3 \cdot 6H_2O$ is similar to the previously described hydrochloric acid extraction process excepting for the method of obtaining the intermediate product $AlCl_3 \cdot 6H_2O$ crystals, the method of decomposing them and recovering the hydrogen chloride so produced, and in the direct use of most of the crystallizer mother liquor as leaching acid. The hydrogen chloride precipitation process includes the following steps illustrated by the attached flowsheet:

(1) Calcination of clay.

(2) Leaching of the calcine at atmospheric pressure at boiling with slightly greater than the stoichiometric amount of approximately 25-27% hydrochloric acid.

(3) Separation, washing, and rejection of the acid-insoluble component (primarily silica) of the clay.

(4) Removal of dissolved iron from the leach liquor by a solvent extraction process which regenerates and recycles the organic extractant.

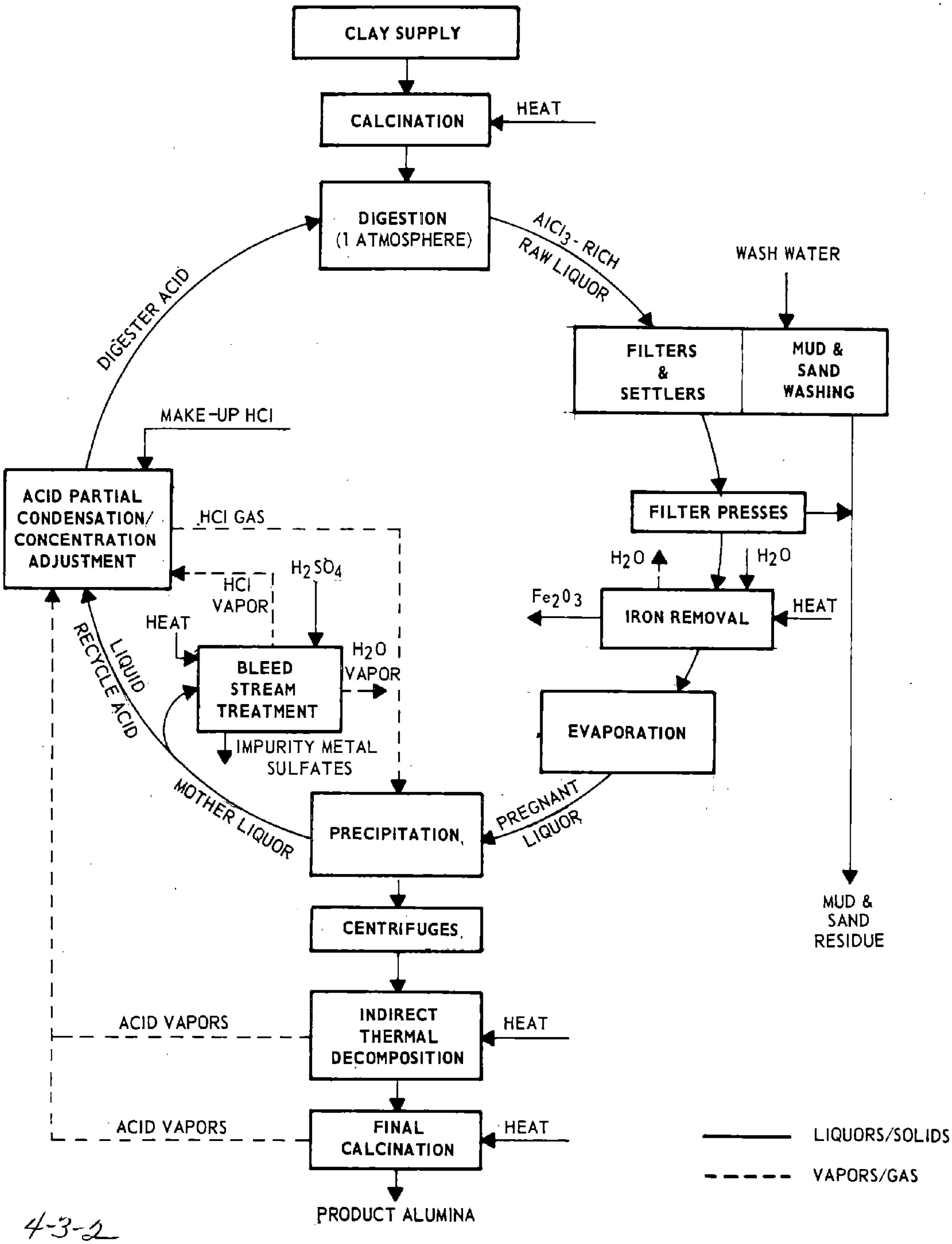
(5) Concentration by evaporation of the solution from which the iron has been removed.

(6) Dissolving under carefully controlled conditions hydrogen chloride gas into the concentrated solution of aluminum chloride to selectively crystallize $AlCl_3 \cdot 6H_2O$, thereby separating the aluminum from dissolved minor constituent metals.

(7) Thermally decomposing the $AlCl_3 \cdot 6H_2O$ crystals. Most of the decomposition must be accomplished in indirectly fired equipment in order to recover the hydrogen chloride substantially free of inerts, although a final direct-fired stage of decomposition may be employed.

FIGURE 4-3-1

ALUMINA FROM CLAY VIA EXTRACTION HCl PRECIPITATION



(8) Withdrawing and treating a fraction of the crystallizer mother liquor to recover dissolved aluminum chloride and hydrogen chloride and to reject soluble impurities and water. The soluble impurities are rejected as anhydrous waste solids.

(9) Recovering by partial condensation concentrated acid for washing the intermediate product $AlCl_3 \cdot 6H_2O$ crystals and simultaneously recovering hydrogen chloride gas substantially free of inerts for recycle to crystallization.

(10) Combining the remaining major fraction of the mother liquor with other liquid and vapor streams and removing heat so as to prepare the acid required for recycle to leaching and hydrogen chloride gas substantially free of inerts for crystallization.

(11) Conversion of iron chloride removed from the process to solid ferric oxide with recovery of its contained chloride as hydrogen chloride.

The process being evaluated has been constructed from information derived from older U. S. Bureau of Mines Reports of Investigation, a recent USBM Report of Investigation RI 8188 describing a new solvent extraction process for iron removal, information published in the older open literature, Kaiser Aluminum experimental work, and Kaiser Aluminum experience.

It is probable that alumina meeting reduction-grade chemical purity and physical property specifications can be manufactured from clay via hydrochloric acid extraction and hydrogen chloride precipitation. The estimated net thermal energy requirement to process is 23.5×10^6 Btu/ton product alumina which probably can be reduced somewhat by further study and engineering design for waste heat recovery. A primary reason for the relatively low energy requirement of this process is that the mother liquor remaining after separating the intermediate product $AlCl_3 \cdot 6H_2O$ crystals becomes, after diversion of whatever bleed stream is taken for the control of soluble impurities other than iron, and after a minor adjustment in concentration, leach acid without distillation. Other factors contributing to a low overall thermal energy requirement are that aluminum chloride crystallizes as a hexahydrate rather than a higher hydrate, and the initial production of a somewhat more concentrated leach liquor which is a consequence of leaching with 25-27% leach acid.

All of the thermal energy required for steam generation, for the indirectly fired thermal decomposition of $AlCl_3 \cdot 6H_2O$ and for the direct-fired concentration and decomposition of waste products may be furnished by any economical fuel, including coal. The process evaluation is based upon the use of oil as fuel in the calcination of clay, but with some development work it is anticipated that this requirement could also be met with powdered coal. A small amount, presently unknown, of clean fuel such as oil may be required in the final calcination of the product alumina.

One major technological problem requires solution before design of a demonstration plant can be undertaken with a reasonable probability of economically successful operation. This is the endothermic thermal decomposition of $AlCl_3 \cdot 6H_2O$ to product alumina which must be carried out substantially, but not entirely, to completion using indirect heat in order to avoid mixing the hydrogen chloride so produced with combustion products. There is reason to believe that the design of industrial scale, indirectly heated decomposition equipment that will operate satisfactorily at an acceptable maintenance cost is possible; but the information required for such a design is not available today.

Other process sections would benefit from the availability of additional engineering design information. These are clay calcination, solid-liquid separation, crystallization, and bleed stream treatment.

Hydrochloric acid losses can be held to low levels, and solutions for environmental protection problems are available.

4.3.2 Background

All of the salient characteristics of hydrochloric acid as an extractant that were discussed in Section 4.2 of the "Technical Appraisal: Alumina from Clay Via Hydrochloric Acid Extraction - Evaporative Crystallization" apply equally to hydrogen chloride precipitation (and so will not be listed again here), but there is one very important addition.

F. A. Gooch discovered and in 1896 obtained U. S. Patent No. 558,725 covering the crystallization of $AlCl_3 \cdot 6H_2O$ from concentrated solutions of aluminum chloride by dissolving hydrogen chloride gas into the solutions. Gooch also proposed recycling the mother liquor (hydrochloric acid) remaining after crystallization back to leach more aluminum although his and subsequent efforts to utilize his discovery failed, because there was no way--other than distilling all of the mother liquor--to separate iron. Gooch and subsequent investigators were also beset with what were in those times insuperable materials of construction, heat transfer, and materials handling problems--particularly in attempting an indirectly heated decomposition of the $AlCl_3 \cdot 6H_2O$ crystals. The last serious investigation of the extraction of alumina from clay with hydrochloric acid and utilizing hydrogen chloride-induced crystallization of $AlCl_3 \cdot 6H_2O$ that has been published took place during World War II.

Recently developed solvent extraction technology has provided a means of separating iron at an acceptable cost. Vapor-liquid equilibrium data for the system HCl-H_2O plus dissolved metallic chlorides have been determined and published. Extensive thermodynamic data on the system HCl-H_2O and metallic chlorides have become available. Much has been learned about heat transfer and solids handling. Metal alloys resistant to HCl and H_2O vapors at elevated temperatures have been developed. Some metals and many other materials have been developed to withstand the corrosive action of aqueous hydrochloric acid and metal chlorides. The hydrochloric acid extraction-hydrogen chloride precipitation process evaluated here is built upon the efforts of the early investigators. It draws upon newer technology and more recently available data in an attempt to solve previously extremely difficult problems, all with the goal of producing alumina at the lowest possible cost.

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4.3.3 The Process

4.3.3.1 Summary

This process employs 25-27% hydrochloric acid for leaching instead of the approximately 20% acid used with evaporative crystallization and therefore produces a somewhat more concentrated leach liquor requiring less evaporation. Otherwise, clay calcination, leaching, solid-liquid separation, tailings disposal, solvent extraction, iron extract treatment, and concentration by evaporation of the primary liquor stream to saturation are identical for the two hydrochloric acid processes. Saturated iron-free liquor enters a two-stage crystallization step in which hydrogen chloride gas is dissolved in the liquor under carefully controlled conditions to greatly reduce the solubility of aluminum chloride, thereby causing the crystallization of $AlCl_3 \cdot 6H_2O$. The crystals are washed free of adhering mother liquor with 35% wash acid and then subjected to an indirectly fired thermal decomposition removing at least 90% of the combined chloride. The decomposition to reduction-grade alumina may be completed with indirect heating in the presence of steam or with direct heat using a low-sulfur, ash-free fuel.

Concentrated acid for crystal washing and hydrogen chloride gas for crystallization are produced by partial condensation of the concentrated vapors from indirectly fired decomposition. All dilute acid vapors, including those from the final direct calcination, are recovered in a separate absorber. Crystallizer mother liquor, less the bleed stream taken for the control of soluble impurities other than iron, provides after blending, with other liquid and vapor HCl-bearing streams, the acid recycled to leaching together with the remainder of the hydrogen chloride gas required for crystallization.

The bleed stream is subjected to further crystallization at higher hydrogen chloride concentration for the recovery of dissolved aluminum chloride. Subsequently, its treatment is substantially the same as previously described for the evaporative crystallization process.

4.3.3.2 Clay Calcination

Entering clay is calcined in the same manner as for processes employing nitric or sulfurous acids as the aluminum extractant.

All of the comments made in the evaluations of the processes employing those acids as extractants--and in particular about the possible development of fluidized solids clay calcination--apply equally when employing hydrochloric acid as the extractant.

4.3.3.3 Leaching

The leaching operation--except for the use of somewhat more concentrated acid containing some recycled dissolved aluminum chloride, which therefore will produce a more concentrated solution of aluminum chloride than if 20% acid without recycling aluminum chloride is used as the extractant--is the same as previously described in Section 4.2 of hydrochloric acid extraction--evaporative crystallization. All previous comments apply.

4.3.3.4 Solid-Liquid Separation

The solid-liquid separation operation is expected to be the same for either variation of hydrochloric acid extraction. The previous description and comments apply.

4.3.3.5 Iron Removal

The previously described iron removal step, and the processing to convert the iron extract to solid iron oxide, are the same as described for evaporative crystallization. The previous description and comments apply.

4.3.3.6 Evaporation

Approximately 1.9 mass units of water/unit product alumina, along with all of the free dissolved HCl, are removed by evaporation from the iron-free leach liquor (including diluted leach liquor recovered by washing the waste solids) to produce a 31% solution of aluminum chloride. The evaporation may be carried out under reduced pressure in order to utilize heat recoverable in other sections of the process. The technology of the evaporative process is well known and should not require much additional development work.

4.3.3.7 Crystallization

Hydrogen chloride gas dissolves readily over a useful range of temperatures at a pressure of one atmosphere or less into aluminum chloride solutions. Starting with a 31% solution of aluminum chloride solution, $AlCl_3 \cdot 6H_2O$ is crystallized as hydrogen chloride dissolves so as to maintain a virtually constant molality in the solution with respect to chloride until the aluminum chloride solubility is depressed to approximately 6.5% in the presence of 25.6% HCl. The solubility of aluminum chloride may be further depressed to 0.7% at 35.5% HCl. The solubility of aluminum chloride changes very little with change in temperature although the equilibrium partial pressure of hydrogen chloride in contact with aluminum chloride solutions changes very rapidly with change in temperature. The solubility of potassium chloride in solutions containing approximately 25% HCl and saturated with $AlCl_3$ is approximately 2% and that of sodium chloride is about 1%. The solubilities of calcium and magnesium chlorides are depressed by the addition of HCl but remain quite high. The solubilities of other metallic chlorides which form complexes tend to increase with increasing concentrations of hydrogen chloride. Existing data are of doubtful applicability to the complex system produced by the cyclic leaching of naturally occurring clay. The industrial application of hydrogen chloride induced crystallization of $AlCl_3 \cdot 6H_2O$ will benefit from the development of further knowledge about solubility relationships in complex liquors.

Struthers-Wells Corporation representatives have stated that because of the concentration-growth-nucleation relationship existing in the crystallizer, it will not be economically practical to produce $AlCl_3 \cdot 6H_2O$ crystals of a useful particle size distribution below a concentration of about 6.5 weight % aluminum chloride. This concentration corresponds to recovery as crystals of about 85% of the dissolved aluminum chloride entering crystallization and has been chosen as the operating condition for this evaluation. Struthers-Wells has also suggested carrying out the crystallization in at least two stages in order to hold the solids content of the slurries at easily manageable levels.

Struthers-Wells has operated, on a small pilot scale as a part of the miniplant program, the hydrogen chloride crystallization of

$AlCl_3 \cdot 6H_2O$. They were able to produce good crystals of controlled particle size distribution and were optimistic about scale-up crystallization operation.

Very little quantitative data is available in regard to the concentration of various impurity metal chlorides which may be present in the mother liquor during crystallization without incorporation of these impurities into the crystals to such an extent that alumina produced from the crystals would not meet chemical purity specifications. It may be inferred from the older literature that adequately pure crystals of $AlCl_3 \cdot 6H_2O$ can be produced in the presence of rather substantial amounts of impurities and that reduction-grade alumina purity specifications can be met if the crystals are washed so as to remove adhering mother liquor adequately.

4.3.3.8 Crystal Recovery

The $AlCl_3 \cdot 6H_2O$ crystals may be separated from the crystallizer mother liquor by either the use of centrifuges or by vacuum filtration. Both the mother liquor and the wash acid will have substantial vapor pressures at the filtration temperature. It will probably be desirable to use a centrifuge in order to eliminate any possibility of flashing and to reduce the quantity of wash acid adhering to the crystals to the lowest possible value. The centrifuge or filter will have to be totally enclosed, and provision will have to be made either for recirculating air drawn through the cake or for scrubbing HCl from the air before discharging it to the environment.

Mother liquor washed from the crystals in admixture with wash acid is conveniently sent to leach acid preparation where the mixture is blended and partially stripped as it becomes part of the recycle leach acid.

Design of the crystal recovery and acid washing section of a demonstration plant is not expected to require any substantial amount of further development work.

4.3.3.9 Decomposition

The crystals next pass to thermal decomposition. $AlCl_3 \cdot 6H_2O$ crystals decompose very rapidly when heated to temperatures above 375°F approximately in accordance with the reaction

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$$2AlCl_3 \cdot 6H_2O \longrightarrow Al_2O_3 + 6HCl\uparrow + 9H_2O\uparrow$$

but the decomposition only proceeds within a reasonable time to a composition of residual chloride <0.1% when a final calcination temperature of approximately 1,650°F is attained. The presence of a high partial pressure of steam facilitates removal of the chloride.

The thermal decomposition process requires approximately 14.5×10^6 Btu/ton product alumina assuming that the alumina and the gaseous products exit at 600°F. No provision is included in the above requirement for steam that may be supplied in the final stage(s) of decomposition.

It is necessary that at least approximately 90% of the decomposition be carried out without mixing combustion products with the vapors produced by decomposition, which overall will contain approximately 57.4% HCl and 42.6% H_2O vapor. This is necessary so that hydrogen chloride in excess of requirements for partial condensation yielding clean 35% wash acid--and for preparation of recycle leach acid--may be directly recovered as hydrogen chloride gas free of inerts suitable for direct recycle to crystallization.

Little information is available with respect to the rate and mechanism of the thermal decomposition process as a function of temperature. A search must be made for materials of construction for heat transfer surfaces that will give satisfactory service at various temperatures above the dew point. Several metals, including zirconium and even aluminum appear to offer corrosion resistance at temperatures not much higher than the dew points for aqueous systems containing their metallic chlorides. High nickel-chromium content metals appear to offer corrosion resistance, as well as mechanical strength at higher temperatures.

It may be necessary to complete the decomposition of the $AlCl_3 \cdot 6H_2O$ at a temperature high enough so that no practical material having adequate mechanical strength with suitable resistance to corrosion will be available for use as a heat transfer surface. In this case it will be necessary to use a direct-fired fluid bed for the last stage of calcination. It is known that the presence of an atmosphere comprising primarily steam lowers the temperature necessary, at a constant decomposition time, to reduce the chloride level to a given value.

It is believed, taking all of the foregoing into consideration, that the design of industrial-scale indirectly heated decomposition equipment is possible, but no such equipment suitable for the decomposition of $AlCl_3 \cdot 6H_2O$ is known to be commercially available today. Information required for the engineering design of an indirectly fired decomposer must be developed before the design of a demonstration plant employing hydrogen chloride precipitation can be undertaken with confidence.

4.3.3.10 Acid Recovery

The acid recovery operation comprises three sections: a wash acid preparation section producing 35% wash acid and HCl gas for use in crystallization; a leach acid preparation section which produces leach acid and hydrogen chloride gas; and a dilute HCl condensation section which condenses low HCl content vapors, either in the absence or presence of combustion products, to obtain a liquid acid containing approximately 20% HCl.

(1) Partial Condensation to Obtain Concentrated Acid Plus Hydrogen Chloride Gas

The vapor stream from the indirectly heated decomposer containing approximately 57% HCl is divided between the leach acid and wash acid preparation sections. The part of it entering the wash acid preparation section passes countercurrently to 25% acid, in a direct contact partial condenser. The acid stream is heated to 220°F by selective condensation of the vapor so that the vapor stream exiting the partial condenser contains 90% HCl and 10% H_2O. The 220°F acid is externally cooled to 175°F. The vapor stream plus the net production of acid from this condenser are fed concurrently to a cooled falling film absorber producing 35% acid at 140°F and 98% HCl gas. This gas returns to crystallization; and the acid is used for washing $AlCl_3 \cdot 6H_2O$ crystals.

(2) Leach Acid Preparation

Used wash acid, concentrated HCl vapors from bleed stream treatment, acid of 10-20% concentration that may be available, and the recycling mother liquor are blended with the remainder of the concentrated HCl vapor that was not used to prepare wash acid. The heat content of the vapor is utilized by controlling heat removal from the system to prepare as a bottom product hot liquid acid containing the amount of dissolved hydrogen chloride desired for recirculation to leaching, and as a top product the balance of the hydrogen chloride gas required in crystallization.

The leach acid preparation section consists of two direct contact packed towers. The concentrated vapors enter the bottom of the first of these, which is irrigated by a recirculating stream of cooled leach acid, plus used wash acid. Partial condensation/stripping occurs to produce 91% hydrogen chloride gas as a top product and an excess of 25% leach acid as the bottom product.

External cooling must be used to remove the heat developed by condensation of HCl and H_2O vapors.

Vapors exiting the first tower enter the second one, which is irrigated with the used wash acid before this acid joins the crystallizer mother liquor in irrigating the first tower. The second tower functions almost adiabatically. The top product from this tower is 99% hydrogen chloride gas, which meets the balance of the requirement for crystallization.

(3) Dilute Acid Condensation

Vapors from the direct contact evaporation/decomposition of waste chloride solutions pass to a dilute acid condenser in which they pass countercurrently to a film of descending dilute acid on the inside of externally cooled tubes.

The exact ratio H_2O:HCl is not presently known for the dilute HCl streams to be dealt with so it has been assumed that the HCl content of these gases may be recovered as 10% acid.

4.3.3.11 Bleed Stream Treatment

A portion of the filtrate from the final stage of intermediate product $AlCl_3 \cdot 6H_2O$ crystallization is withdrawn from the process for the control of soluble impurities other than iron. It is estimated that withdrawal altogether of approximately 5% of the final crystallizer mother liquor (filtrate) will be required.

The first treatment of this stream is saturation with hydrogen chloride gas at 120°F to reduce the solubility of $AlCl_3$ below 1%. The $AlCl_3 \cdot 6H_2O$ crystals obtained will not meet particle size nor purity specifications for feed to decomposition but will be filterable. They are filtered, recovered, and redissolved in the iron-free leach liquor proceeding to evaporation.

Further treatment of the filtrate has three functions:

(1) rejection of soluble impurities other than iron from the process;

(2) recovery of the HCl contained in the filtrate; and

(3) rejection of water from the process.

The washings are mixed in a stripping column with a hot, concentrated, recycling stream of previously separated waste alkali and alkaline earth metal chlorides, so as to prepare after mixing--on an HCl-free basis--a solution approximately 55% H_2O and 45% waste chlorides. The presence of the high metal chloride concentration is known to greatly increase the volatility of the HCl in relation to H_2O, the latter having a great affinity for the dissolved $MgCl_2$ and $CaCl_2$. Almost pure HCl vapor exits the top of the column, whereas the bottom liquid contains little HCl but nearly all of the H_2O in the filtrate being processed.

Concentrated HCl vapor from the top of the column passes to the leach acid preparation section of acid recovery. The somewhat diluted waste chloride stream passes to an evaporator where it is reconcentrated to about 50% metal chlorides. The major fraction of the reconcentrated waste chloride stream is recycled to stripping, but the net production is withdrawn for further treatment described below. Acidic water vapor from the evaporator proceeds to the dilute acid condenser for recovery of contained HCl.

The chemical engineering principles involved in the addition of a third component to a two-component system in order to make possible separation of the original two components by distillation are well known. There is reportedly one commercial installation in the U. S. of this method for separating HCl and

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H_2O. Other commercial installations have been reported in Eastern Europe, and a partially analogous operation has been reported in Israel. There appears to very little doubt that the method is operable, but piloting is recommended prior to design of a demonstration plant to solve problems that may arise due to the presence of aluminum chloride, the possible formation of double salts, etc. The pilot study should be based upon a recirculating waste chloride solution of a composition that would be derived from a particular clay.

4.3.3.12 Sulfuric Acid Treatment of Waste Chlorides

The net production of concentrated waste chlorides is treated with sulfuric acid equivalent to the alkali and alkaline earth metals present (but not equivalent to alumina) and calcined. Representative reactions occurring are:

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl \uparrow$$

$$2AlCl_3 + 3H_2O \longrightarrow Al_2O_3 + 6HCl \uparrow$$

The HCl produced is relatively concentrated and is sent to leach acid preparation. The mixture of sulfates and alumina is sent to waste.

The technology of the calcination of chlorides with sulfuric acid to produce metal sulfates plus HCl is well known. No further development work is necessary prior to design of a demonstration plant.

4.3.4 Energy Requirements

The net energy requirements to process for HCl extraction-HCl crystallization are:

	Btu/ton Al_2O_3
Clay calcination	5.3×10^6
Iron removal	1.4×10^6
Evaporation	1.7×10^6
Thermal decomposition	14.5×10^6
Bleed stream treatment	0.6×10^6
TOTAL	23.5×10^6

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The energy requirement for iron removal is based upon the use of conventional multiple effect concentration of the extract, although a substantial reduction in the energy requirement for evaporation may be achieved by methods discussed in Section 4.3.3.10.

Heat required for evaporation is low in this process because of the acid concentration employed in leaching and because the free water in which the $AlCl_3 \cdot 6H_2O$ is dissolved, less the bleed stream, is not evaporated.

The nature of the process requires that the thermal energy intensive $AlCl_3 \cdot 6H_2O$ decomposition be carried to about 90% completion using indirect heat. A concomitant advantage is that relatively inexpensive fuels (including coal) may be used to provide the indirect heat. A maximum of 1.5×10^6 Btu in the form of clean fuel such as oil may be required in a final decomposition stage. The use of direct vs. indirect heating in the final decomposition stage has not yet been decided, and the exact heat requirement in this stage cannot be precisely determined. The process energy balance has been constructed on the basis of 90% indirect heat and 10% direct heat for product decomposition.

Waste heat may be recovered from the condensation of hydrochloric acid by innovative design in the acid recovery section. This heat could be employed in vacuum evaporation to reduce the amount of steam otherwise required, and its utilization will also result in capital savings. Additional heat rejected directly to cooling towers may possibly be utilized on a single-effect basis for evaporation of water from dilute solutions, thus reducing steam requirements. Remaining steam requirements can be met by coal-fired boilers. It is expected that after some development work, entering clay can be calcined using coal as the heat source.

4.3.5 Environmental Control

It will be necessary to construct as a closed system with respect to the environment those plant sections where hydrogen chloride is present in order to safeguard the health of the workmen, avoid excessive maintenance costs, avoid acid losses, and meet anticipated emission standards. Gases containing HCl--including air which has been in contact with acidic chloride solutions--will require wet scrubbing. Fortunately, this is not expected to be difficult or extremely costly because of the extreme affinity of hydrogen chloride for water. Covered leach tanks, for example, can be vented to the atmosphere through a condenser. Filters must be covered, but also can be vented to the atmosphere through a condenser/scrubber. Recovery of hydrogen chloride to meet air pollution control requirements can be assured in the acid recovery section.

Waste solids from leaching will comprise silica, a smaller amount of unreacted clay, and small amounts of unreacted accessory minerals. The silica will not be excessively hydrated and these waste solids should make a good subsoil. It will undoubtedly be desirable to return them to mined-out areas for disposal, and present-day technology makes possible return to the process of chloride values accompanying the waste solids. Small amounts of chloride which may accidentally find its way into the groundwater will be indistinguishable from chlorides which are natural constituents of groundwaters. Other waste solids from the process are iron oxide and a mixture of metal sulfates with alumina. The iron oxide may be disposed of with the leach solids or may have some value. The sulfate-alumina mixture will require disposal in a manner such that the sulfates will not be leached out or where the presence of dissolved sulfate will not be objectionable. The quantity of sulfates produced in relation to alumina will be small.

Heat entering the process is largely rejected to the atmosphere in combustion gas streams or by means of cooling towers. The process does not produce a liquid effluent other than the water present in the waste leach solids.

4.3.6 Alumina Product Quality

Experimental evidence based upon literature reports, some direct laboratory work and some miniplant results, indicate the chemical purity of chloride process alumina with respect to metals has the potential of being considerably higher than Bayer process aluminas. The extent to which chloride may be economically removed from such aluminas, and the actual extent to which reduction plant operations will require its removal, are

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not known with certainty at this time. Phosphate is a material present only in trace quantities in the entering clay. It is not expected to cause difficulty in the hydrochloric acid extraction of alumina from clay, but the P_2O_5 specification in the finished alumina is very low; and very little is known about the passage of phosphate through the processing cycle.

Tests on small quantities of chloride process alumina have shown that it can be produced to meet present day specifications for surface area and water absorption. This alumina also appears to dissolve very readily in molten cryolite. It will be possible to produce $AlCl_3 \cdot 6H_2O$ crystals in a particle size distribution appropriate as the precursor to the finished alumina. Assuming that a decomposition process can be developed which--in addition to meeting other requirements--will minimize attrition, it is probable that the particle size distribution specification can also be met.

4.3.7 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000/d of alumina.

(2) The chemical analysis of the clay feed (dry basis) is as follows:

Al_2O_3	36.5 %
Fe_2O_3	0.86
SiO_2	46.4
L. O. I.	13.54
Other*	2.7
	100.00%

*Other is primarily TiO_2.

(3) The raw clay feed to the process contains 18.5% free moisture.

(4) A rotary kiln is used for the calcination of the clay feedstock.

(5) There is a 1% dust loss (calcined basis) from the rotary kilns used to calcine the raw clay.

(6) 15% of the heat of reaction in the leaching tanks is released in the form of vapors. These vapors contain 1% HCl and are condensed and returned to the leach tanks.

(7) 95% extraction efficiency of Al_2O_3 is achieved in the leaching step.

(8) 95% of Fe_2O_3 is solubilized in the leaching step.

(9) 16.3% of "other" is solubilized in the leaching step. This soluble fraction mainly consists of sodium, potassium, calcium, and magnesium salts, plus phosphates and sulfates.

(10) Approximately 5% excess HCl is contained in the leach acid.

(11) The underflow from the settling and washing units contains 33% solids by weight.

(12) Filter press solids from pregnant liquor polish filtration contains 60% solids.

(13) 1% of the soluble alumina is lost in the leach waste residues.

(14) Chlorine is added to the pregnant liquor before solvent extraction based upon one third of soluble iron content being present as ferrous iron.

(15) 100% of the chlorine added is converted to HCl.

(16) A solution of 10% Alamine 336 in kerosene is used as the organic extractant for ferric iron.

(17) The iron content in the pregnant solution from solvent extraction is reduced to about 0.001 grams per liter.

(18) A volume ratio of aqueous/organic of 3/1 is present during extraction.

(19) A volume ratio of organic/aqueous of 3.5/1 is present during stripping.

(20) The strip acid will contain approximately 0.03% HCl.

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(21) The recycled organic solution to extraction will contain about 0.5 grams per liter Fe.

(22) The organic loss is taken as 2.1 lb per ton Al_2O_3 or 1 ton per day.

(23) Use of the distribution coefficient of .004 for aluminum when using Alamine 336 is equivalent to a loss of 10 tons per day of $AlCl_3$ in the solvent extraction section.

(24) A multiple effect evaporator (3-effect) is used to concentrate the crystallizer feed solution.

(25) The $AlCl_3 \cdot 6H_2O$ crystal slurry from the crystallizers is filtered and washed on centrifuges yielding a cake containing 95% solids.

(26) Mother liquor from centrifugation is recycled to the crystallizer.

(27) The bleed stream for minor impurities purging ("other") is 5% of recycle acid stream.

(28) 0.2 lb of 35% acid wash is used per 1 lb of $AlCl_3 \cdot 6H_2O$ crystals.

(29) The washed $AlCl_3 \cdot 6H_2O$ crystals are decomposed in indirect fired kilns.

(30) There is a 1% dust loss (calcined basis) from the decomposition and calcination of $AlCl_3 \cdot 6H_2O$ crystals.

(31) The product alumina will contain 0.01% residual Cl_2.

(32) Only combustion water has been included in the material balance of direct fired heating units.

(33) 12 ton/d of HCl is lost in the acid recovery section.

(34) The bleed liquor is stripped to remove 93% of free HCl and evaporated in multiple effect evaporators to a 45% solution of chlorides.

(35) Sufficient liquor from the evaporator is recycled to maintain a 40% solution of chlorides in the HCl stripping step.

(36) A stoichiometric quantity of H_2SO_4 for "other" is added before the waste chlorides decomposition.

(37) The stripping solution is concentrated to a 50% solution of chlorides in a multiple effect evaporator before decomposition in a direct fired fluid bed decomposer.

(38) Makeup HCl is added as HCl gas to the acid recovery section.

(39) A 53°F temperature rise occurs in cooling water.

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TABLE 4-3-1

ALUMINA FROM CLAY
HYDROCHLORIC ACID PROCESS/GAS PRECIPITATION
DAILY THERMAL REQUIREMENTS
FOR 1,000 TON/D Al_2O_3

	100 LB/IN^2 (GA) STEAM, M LBS (881 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
CLAY PREPARATION			
CALCINATION	–	5,330	–
LEACHING			
LEACHING CONDENSER	–	–	449
EVAPORATION			
EVAPORATION & CRYSTALLIZING (3-EFFECT)	1,961	–	9,000
DECOMPOSITION & CALCINATION	–	14,500	–
BLEED STREAM PROCESSING			
HCl STRIPPING	273	–	–
EVAPORATION (3-EFFECT)	256	–	–
DECOMPOSITION	–	84	–
STRIPPING SOLUTION PROCESSING			
EVAPORATION (3-EFFECT)	1,175	–	–
DECOMPOSITION	–	378	–
ACID RECOVERY	–	–	10,710
TOTALS	3,665 (3,229 MM BTU)	20,292	20,159

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 23,521 MM BTU/D OR 23.5 MM BTU/TON Al_2O_3

Table 4-3-2 (Sheet 1 of 6)

Alumina from Clay/Hydrochloric Acid Process
Hydrochloric Gas Precipitation
Material Balance

1,000 TON/D Al_2O_3

Process Stream	1a	1b	1c	2	3	4	5	6	8a	8b	8c
Component											
Al_2O_3	1091	1091	1080	1080				11	54		
$AlCl_3$						444			3130.5	2285.5	3101.5
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3	25	25	25	25					1		
$FeCl_3$									49	36	49
HCl						2348			105	77	105
L.O.I.	405	405						405			
H_2O	679	679			4560	6880	6	679	7431.5	5423.5	8950.5
Other	81	81	80	80				1	67		
Other as Soluble Salts						292			311	227	308
SiO_2	1387	1387	1373	1373				14	1373	8	8
Organic											
H_2SO_4											
Cl_2											
Total	3668	3668	2558	2558	4560	9964	6	1110	12522	8057	12522

All units are in short tons per day.

Table 4-3-2 (Sheet 2 of 6)

Alumina from Clay/Hydrochloric Acid Process
Hydrochloric Gas Precipitation
Material Balance

Process Stream	8d	8e	10	11	12	13	14a	14b	15	16	20
Component											
Al_2O_3	54						54				
$AlCl_3$	845	816	3100.5	3090.5	3111	2258.5	29	1	1812		444
$AlCl_3 \cdot 6H_2O$						4820				37	
Fe_2O_3	1						1				
$FeCl_3$	13	13	49								
HCl	28	28	116	116	107	2857			989	1	2006
L.O.I.											
H_2O	2008	3527	8950.5	8950.5	6990	10998	3041	6	6163.5	2	5100
Other	67						67				
Other as Soluble Salts	84	81	308	308	308	630.5	3		322.5		292
SiO_2	1365						1365	8			
Organic											
H_2SO_4											
Cl_2											
Total	4465	4465	12524	12465	10516	21564	4560	15	9287	40	7842

Table 4-3-2 (Sheet 3 of 6)

Alumina from Clay/Hydrochloric Acid Process Hydrochloric Gas Precipitation Material Balance

Process Stream	23	24	25	26	27	28	29a	29b	30	31	32
Component											
Al_2O_3		10	960	1000							
$AlCl_3$											
$AlCl_3 \cdot 6H_2O$	4783		237								
Fe_2O_3											
$FeCl_3$											
HCl	88			1	106			2149	834	1315	512
L.O.I.											
H_2O	163				132	301	52	1688	655	1033	
Other											
Other as Soluble Salts	1		1	1							
SiO_2											
Organic											
H_2SO_4											
Cl_2											
Total	5035	10	1198	1002	238	301	52	3837	1489	2348	512

Table 4-3-2 (Sheet 4 of 6)

Alumina from Clay/Hydrochloric Acid Process
Hydrochloric Gas Precipitation
Material Balance

Process Stream	33	34	35	40	44	47	48	49	50	51	54
Component											
Al_2O_3											
$AlCl_3$						2.5			99.5	97	2.5
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3											
$FeCl_3$											
HCl	1249	1761	30	352	153	125	117	8	8		
L.O.I.											
H_2O				655	420	224.5	2	201	1033.5	811	21.5
Other											
Other as Soluble Salts						15			582	567	15
SiO_2											
Organic											
H_2SO_4											
Cl_2											
Total	1249	1761	30	1007	573	367	119	209	1723	1475	39

Table 4-3-2 (Sheet 5 of 6)

Alumina from Clay/Hydrochloric Acid Process
Hydrochloric Gas Precipitation
Material Balance

Process Stream	55	56	57	58	69	70	71	72	87a	87b	87c
Component											
Al_2O_3	1										
$AlCl_3$											
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3											
$FeCl_3$											
HCl		6			10		10	59	1		1
L.O.I.											
H_2O		24		4	1979	1939	40	305	1021	61	960
Other											
Other as Soluble Salts	14										
SiO_2											
Organic								1			
H_2SO_4			2								
Cl_2											
Total	15	30	2	4	1989	1939	50	365	1022	61	961

Table 4-3-2 (Sheet 6 of 6)

Alumina from Clay/Hydrochloric Acid Process
Hydrochloric Gas Precipitation
Material Balance

Process Stream	89a	89	90	91	92	95	96	97	98	102	111
Component											
Al_2O_3									4		
$AlCl_3$			10		10	10					
$AlCl_3 \cdot 6H_2O$											
Fe_2O_3									24		
$FeCl_3$		6	55		49	49					
HCl				1	1		41			12	
L.O.I.											
H_2O				960	1021	61	64	13		17	
Other											
Other as Soluble Salts											
SiO_2											
Organic	1	3081	3082		1	1	1			1	
H_2SO_4											
Cl_2											11
Total	1	3087	3147	961	1082	121	106	13	28	30	11

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4.3.7 Equipment List

ALUMINA FROM CLAY VIA HYDROCHLORIC ACID EXTRACTION - HCL PRECIPITATION PROCESS

Clay Preparation Area

Belt conveyor under wobbler feeder and primary crusher
Truck dump hopper
Wobbler feeder and hoppers from truck dump
Primary crusher and chutes
Belt conveyor: primary crushers to stockpile
Belt conveyor and distributors for stockpile
Stockpile, enclosure, dust collection system, and reclaim system
Wobbler feeder from stockpile
Belt conveyor, stockpile to hammermills
Hammermills and hoppers
Belt conveyor, hammermills to elevator
Bucket elevators from secondary crusher
Vibrating screens, chutes, and covers
Roll compactors with covers
Belt conveyor compactors to elevators
Belt conveyor screens to raw clay surge bin
Raw clay surge bin
Weigh belt feeders
Belt conveyors raw clay surge bin to kilns
Rotary kilns
Apron feeders with covers from coolers
Calcine bucket elevators
Calcine vibrating screens and chutes
Calcine cage mill grinder with covers
Calcine apron feeder with cover
Bucket elevator to calcine storage bins
Calcine storage bins
Weigh belt feeders to leaching
Belt conveyors to leach tanks
Dust collection system

Leaching, Thickening, CCD Washing, and Filtration Area

Leach tank screw feeders
Leach tanks (lined)

EQUIPMENT LIST (Cont)

Leach tank agitators
Leach tank recirculating pumps
Leach tank vapor condensers
Leach flash tanks (lined)
Leach slurry pumps
Flash vapor condensers
Leaching condensate tanks and ejectors
Leaching condensate pumps
Dilute HCl transfer pumps
Sand thickener tanks (lined and coverd)
Sand thickener rake mechanishms
Sand thickener underflow pumps
Sand thickener overflow pumps
Sand washer tanks (lined and covered)
Sand washer rake mechanisms
Sand washer underflow pumps
Sand washer overflow pumps
Sand slurry tank (lined)
Sand slurry pumps
Flocculant prep system (HNO_3)
Filter aid system (HNO_3)
Filter presses
Vibrating screens
Press cake relay tanks
Filtrate tanks
Filtrate pumps
Repulped slurry pumps
In-line chlorine blender
Collecting sluice
Spent filter and dumpers
Filter aid storage tank
Filter aid conveyor and weigh feeder
Filter aid slurry tanks
Filter aid slurry tank agitators
Filter aid slurry pumps
Filter aid liquor pumps

Fe Removal, Stripping, $FeCl_3$ Evaporation Decomposition Area

Solvent surge tank (lined)
Solvent surge tank pumps

EQUIPMENT LIST (Cont)

Head tanks
Mixer settlers
Mixer settler covers
Loaded solvent pumps
Mixing pumps and baffles
Raffinate pumps
Raffinate storage tank (lined)
Raffinate storage pumps
Loaded solvent surge tank (lined)
Loaded solvent surge tank pumps
Regenerated solvent pumps
Wash water tank
Wash water tank pumps
Spent $FeCl_3$ pumps
$FeCl_3$ solution tanks
$FeCl_3$ solution tank pumps
Decanol unloading pump
Kerosene unloading pump
Alamine unloading pump
Decanol storage tank
Kerosene storage tank
Alamine storage tank
Decanol blending pumps
Kerosene blending pumps
Alamine blending pumps
Solvent blend tank
Solvent make-up pumps
$FeCl_3$ multiple-effect evaporator system
$FeCl_3$ evaporator condensers
$FeCl_3$ decomposer system

Pregnant Liquor Evaporation, Crystallization, and Centrifuging Area

Pregnant liquor evaporation system
Feed preheaters
Circulating heaters
Circulating pumps
Transfer pumps
Evaporator hotwell
Evaporator hotwell pumps
Evaporator cooling tower
Evaporator cooling tower sump

EQUIPMENT LIST (Cont)

Spray scrubber pumps
Cooling tower pumps
Two-stage crystallizer systems
Coolant circulating pumps
1st stage crystallizer product pumps
2nd stage product pumps
1st stage crystallizer product centrifuges
2nd stage crystallizer product centrifuges
1st stage centrate tanks
2nd stage centrate tanks
Hydroclones
1st stage centrifuge wash tanks
2nd stage centrifuge wash tanks
1st stage centrate pumps
2nd stage centrate pumps
Centrifuge wash pumps
$AlCl_3 \cdot 6H_2O$ crystal bins
Weigh feeders
Recycle crystal slurry tank
Slurry tank agitator
Recycle crystal slurry pumps
1st stage centrifuge conveyors
2nd stage centrifuge conveyors
Crystals conveyors to decomposition
Centrifuge discharge transfer conveyors

$AlCl_3 \cdot 6\ H_2O$ Decomposition Area

Decomposer feed screw conveyor
Stage 1 decomposer
Stage 1 cyclone
Stage 1 recirc. blower
Stage 1 decomposer heal coils
Product hopper and rotary valves
Stage 1 decomposer heating system
Stage 1 decomposer ash handling
Stage 2 decomposer
Stage 2 cyclone
Stage 2 recirc. blower
Stage 2 heat coils
Product hopper and rotary valves

EQUIPMENT LIST (Cont)

Stage 2 decomposer heating system
Stage 2 decomposer ash handling
Stage 1 and 2 coal pulverizers
Stage 1 and 2 precipitators
Stage 1 and 2 SO_2 scrubbers
Flash calciner
Calciner cyclone
Stage 3 decomposer
Stage 3 cyclone
Oil burners
Product hopper and rotary valves
Fluid bed cooler
Cooler cyclone
Air blower
Alumina conveying system (2)
Alumina silo (2)

Leach Acid Preparation, Wash Acid Preparation, and Dilute HCl Recovery Area

Leach acid absorber column (packed and lined)
Intermediate cooling heat exchangers
Intermediate cooling recirculating pumps
Vapor product blowers
Liquid product recirculating pumps
HCl storage tanks
Air padding for HCl unloading
HCl solution make up pumps
Falling film absorbers
Falling film absorbers vapor product blowers
Falling film absorbers liquid product pumps
Falling film absorbers liquid product heat exchangers
Wash acid absorption towers (lined and packed)
Wash acid absorption towers circulating pumps
Dilute acid gas waste heat recovery boiler
Dilute acid gas cooler
Dilute acid gas falling film absorber
Dilute acid gas falling film absorber product pumps
Water spray for combustion gases (lined and packed)

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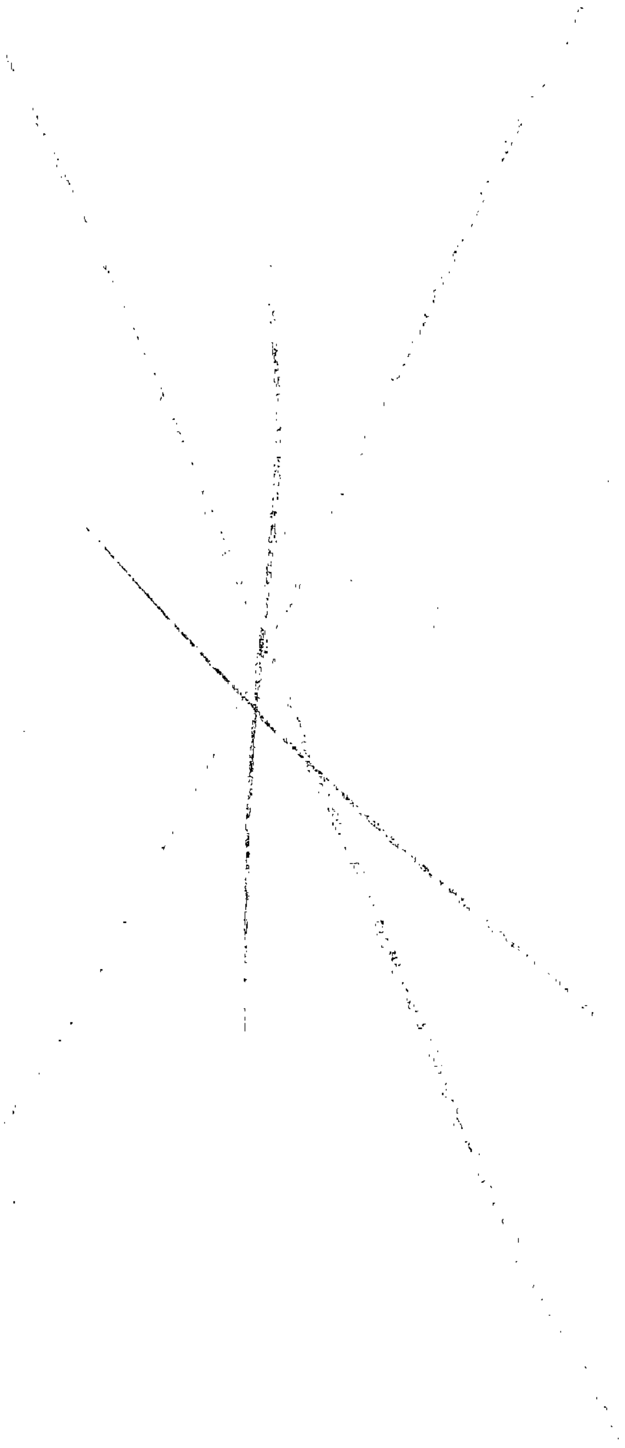
EQUIPMENT LIST (Cont)

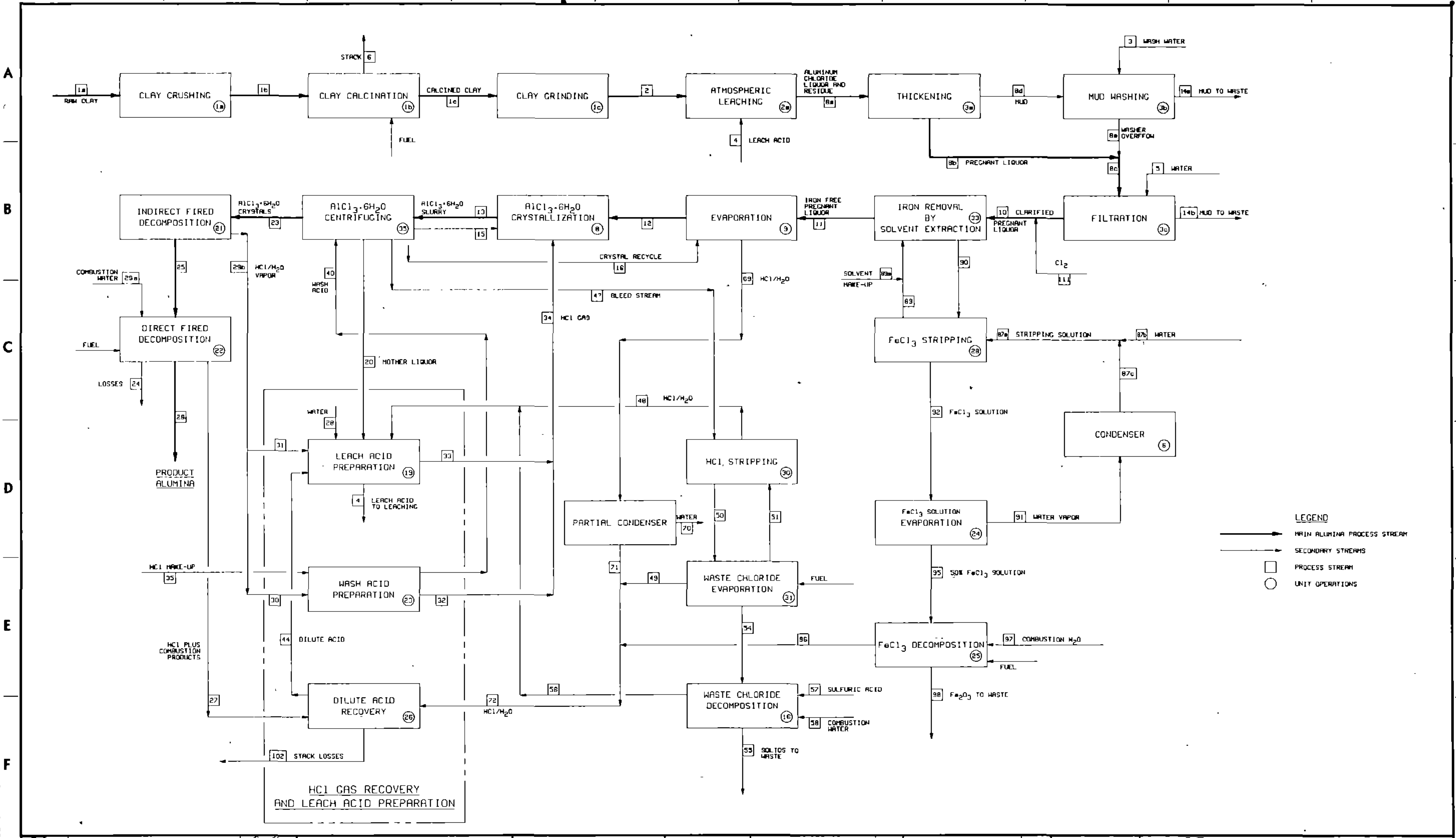
Bleed Stream Crystallizer System Area, Stripping, Evaporation, Decomposition

Bleed stream crystallizer system
Bleed stream crystallizer coolant circulating pumps
Bleed stream crystallizer heat exchanger
Bleed stream crystallizer product pumps
Bleed stream crystallizer hydroclones
Bleed stream crystallizer centrifuges
Bleed stream crystallizer centrate tank (lined)
Bleed stream crystallizer centrate pumps
Bleed stream crystallizer crystal slurry bins (lined)
Bleed stream stripper (lined and packed)
Bleed stream stripper reboiler
Bleed stream stripper underflow pumps
Bleed stream direct contact evaporator (lined and packed)
Bleed stream evaporator underflow pumps
Bleed stream evaporator burner system
Bleed system decomposer (Mannheim furnaces)
Waste apron feed
Solid waste pit
Solid waste pit agitator
Solid waste pit pumps

Utilities

Steam plant and auxiliary systems
Cooling tower and auxiliary systems





FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-3-2

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-3-1

NOTES

NO	DATE	REVISION	BY	APP	APP

DESCRIPTION COST ACCOUNT

WORK COVERED BY THIS DRAWING CHARGED TO COST ACCOUNT ABOVE

CONSTRUCTION APPROVAL

APPROVAL DATE

SCALE:
DESIGNED BY
DRAWN BY ADS
CHECKED BY
APPROVED BY
APPROVED BY
DATE

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO. J0265048

ALUMINA FROM CLAY
HYDROCHLORIC ACID PROCESS
HCl GAS INDUCED CRYSTALLIZATION

JOB No. 76161-001
FIGURE NO. 4-3-2
REVISION R-0

NOT REPRODUCIBLE

4.4 SULFUROUS ACID/CLAY

~~4.4 TECHNICAL APPRAISAL:~~ ALUMINA FROM CLAY VIA SULFUROUS ACID EXTRACTION

4.4.1 Summary and Conclusions

Overall, sulfurous acid extraction must be viewed as a head-end treatment for the removal of silica from clay to render it amenable to refining into reduction-grade alumina by a modified Bayer process. The head-end treatment does make possible certain cost reductions in the subsequent modified Bayer refining process.

The process by which this is accomplished is illustrated in summary form on the following page and includes the following steps:

(1) Calcination of clay.

(2) Leaching of the calcine for 15 hours on a semicontinuous basis at 130°F and 9 atmospheres pressure.

(3) Removal of excess SO_2 and reduction of the pressure to atmospheric in a blowdown tank.

(4) Separation, washing and rejection to disposal of the acid-insoluble component (primarily silica) of the clay.

(5) Autoclaving at 212°F and 3 atmospheres pressure the aluminum-bearing solution in order to precipitate semicrystalline, filterable aluminum monobasic sulfite.

(6) Thickening at atmospheric pressure the resulting slurry. Approximately 55% of the solution as overflow recycles to leach acid preparation.

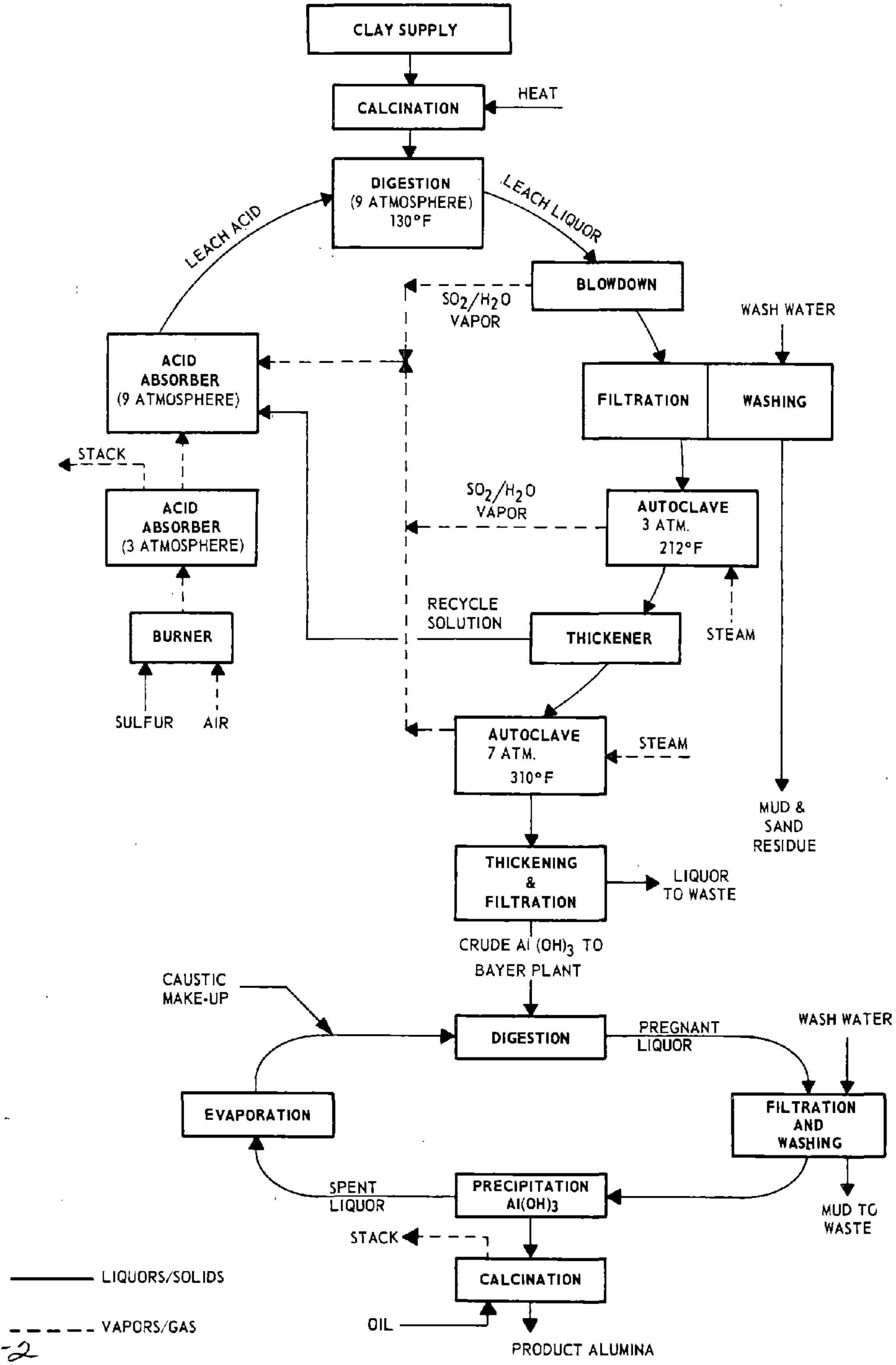
(7) Autoclaving the thickener underflow at 310°F and 7 atmospheres pressure to decompose the aluminum basic sulfite, forming crude alumina trihydrate which retains the crystalline form of the basic sulfite and is filterable.

(8) Thickening and filtering the crude alumina trihydrate.

(9) The crude alumina trihydrate goes to further refining in a modified Bayer process to refine it to reduction-grade quality. The solution goes to waste or waste treatment.

FIGURE 4-4-1

ALUMINA FROM CLAY VIA SULFUROUS ACID EXTRACTION



The technical evaluation of the process sections prior to the modified Bayer process final refining are based upon a U.S. Bureau of Mines study of previously published German investigations and older patent literature, a Kaiser review of the published German investigation, and a private communication from one of the original German investigators.

There is very little question that the modified Bayer refining process, which is the final step in the extraction of alumina from clay via sulfurous acid, will produce reduction-grade alumina meeting every specification for and interchangeable with Bayer process alumina derived from bauxite. The estimated energy requirement however, including the Bayer refining, is approximately 28.2×10^6 Btu/ton alumina as net to process. This is not believed to be substantially reducible in view of the intensive effort already put into development of the process. Included is 3.9×10^6 Btu for final calcination of trihydrate which must be supplied in the form of a clean fuel such as oil. The remainder of the energy requirement may be supplied by the combustion of any fuel, including coal.

Sulfur dioxide is an environmentally objectionable gas only moderately soluble in water. It will be very difficult to avoid losses of this gas from a pressurized system. Sulfur may be easily changed from one valence state to another. Sulfur dioxide is easily converted to elemental sulfur, sulfate, and other compounds. Sulfur consumption, due primarily to the conversion of sulfur dioxide to other compounds, is therefore 20% of alumina produced. The loss of sulfur will cause air and water environmental problems difficult and costly to control. There does not appear to be any way to avoid the loss of sulfur and attendant problems because of the chemical nature of sulfur. Some of the sulfur is converted to finely divided elemental sulfur dispersed in the crude alumina trihydrate. The trihydrate will also contain residual soluble sulfate and perhaps other sulfur compounds. The presence of these impurities will cause difficulties in the modified Bayer final refining process, and research and development effort will be required to solve the difficulties. No technical problems are otherwise expected in the Bayer refining process.

The extraction of alumina from clay with sulfurous acid has received intensive study in the past. There is no known body of new technology which, if applied to sulfurous acid extraction, could result in a major cost reduction. It is concluded that the process as it exists is approaching the maximum state of development.

4.4.2 Background

The extraction of alumina from clay by means of sulfurous acid has interested many investigators since the latter part of the 19th Century because:

(1) Sulfurous acid is probably the cheapest acid industrially available.

(2) Acid consumed in reaction with iron can be recovered relatively easily.

(3) Aluminum sulfite may be decomposed hydrothermally at 320°F at a comparatively low energy requirement.

Sulfurous acid extraction of clay was carried to its greatest development in Germany, probably because of the unavailability of bauxite there during World War I and anticipation of the same problem in World War II. Sulfurous acid extraction was developed to the point where 8,000 tons/yr alumina were reportedly manufactured there during World War II.

The literature describing the German process is primarily a series of U. S. patents which were issued beginning in the 1930's extending through 1941, an excellent description in Fulda-Ginsberg, and some older references tabulated therein. F. A. Peters, P. W. Johnson, and R. C. Kirby have translated the appropriate section of Fulda-Ginsberg. They have used the German experience, the patent literature, and the older references as the basis of U. S. Bureau of Mines Report of Investigations No. 5997, "An Evaluation of the Sulfurous Acid-Caustic Purification Process". There is no known recent published work on sulfurous acid extraction of clay other than one or two Russian papers containing very little information. The process evaluated here is fundamentally the same as the one described in considerable detail in USBM RI No. 5997. The only part of the process description to be given here therefore will be that which is pertinent to the present technical appraisal.

4.4.3 The Process

4.4.3.1 Summary

Clay entering the process is calcined at 1,300°F to chemically activate it, remove free and combined water, and destroy any organic materials which may be present. The calcine is digested with about 20% sulfurous acid for about 15 hours at 9 atmospheres to dissolve 75-80% of the contained alumina. The pressure is relieved, excess sulfur dioxide returned to leach acid preparation, and the liquor filtered away from the insolubles. The latter, after washing, are sent to disposal.

The pregnant liquor, including the washings, is autoclaved at 212°F under 3 atmospheres SO_2 pressure, which causes the precipitation of a semicrystalline basic sulfite. The slurry is thickened, with 55% of the liquid as overflow being returned to the acid absorber for eventual recycle as leach acid. The thickener underflow passes to a second autoclaving at 310°F with steam being passed through the autoclave at 7 atmospheres. Under this treatment the basic sulfite decomposes to a filterable alumina trihydrate which retains the crystalline form of the basic sulfite, and sulfur dioxide leaves in the steam. The trihydrate slurry is thickened and filtered. The crude alumina trihydrate goes to a modified Bayer process final refining operation. The waste liquor, containing soluble sulfur compounds in which the sulfur exists in various valence states, is discarded or sent to treatment for environmental control purposes.

Makeup sulfur dioxide is supplied by burning elemental sulfur with air and absorbing the sulfur dioxide in water at 3 atmospheres pressure. The resulting sulfurous acid is pumped into the primary acid absorber/leach acid preparation section, which operates at 9 atmospheres pressure.

4.4.3.2 Calcination

Raw clay is brought into the process and calcined as described in the technical evaluation of the nitric acid process. It would be particularly advantageous in sulfurous acid leaching (because sulfurous is a weak acid and the yield of alumina was always relatively poor) to be able to use fluidized solids clay calcination.

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Fluidized solids clay calcination--assuming that problems associated with it and described in the nitric acid section can be overcome--is probably the most important development in processing technology applicable to sulfurous acid extraction since the World War II German effort. However, the energy requirement and cost estimates are based upon use of a rotary kiln for the calcination in order to rely on existing technology.

4.4.3.3 Quench

The oxidation of S^{+4} to S^{+6} by the reaction

$$SO_3^{=} + 1/2\ O_2 \longrightarrow SO_4^{=}$$

or by the disproportionation reaction

$$2H^+ + 3SO_3^{=} \longrightarrow 2SO_4^{=} + S^o + H_2O$$

is a continuing problem throughout most of the steps in the manufacture of alumina via sulfurous acid extraction. USBM recommends a water quench of the calcined clay for the purpose of eliminating any adsorbed oxygen. It is questionable whether oxygen adsorbs on the calcined clay. If an experimental study of sulfurous acid extraction is undertaken, the need for a quenching step should be determined.

4.4.3.4 Leaching

The overall reactions by which the aluminum is solubilized during leaching are:

$$\underset{\text{gas}}{SO_2} + \underset{\text{liquid}}{H_2O} \rightleftharpoons \underset{\text{solution}}{H_2SO_3}$$

$$\underset{\text{solid-calcine}}{Al_2O_3 \cdot 2SiO_2} + \underset{\text{solution}}{3H_2SO_3} \longrightarrow \underset{\text{solution}}{Al_2(SO_3)_3} + 3H_2O + \underset{\text{waste}}{2SiO_2}$$

although the aluminum is only soluble in the presence of an excess of dissolved SO_2.

Sulfur dioxide has only a limited solubility in water, which decreases rapidly with increasing temperature at one atmosphere pressure. The amount of aluminum sulfite which can remain in solution is a direct function of the dissolved sulfur dioxide concentration. The rate of reaction of the calcined clay decreases with decreasing sulfurous acid concentration but increases with increasing temperature. Silica tends to dissolve in the leach liquor, but silica solubility is depressed with increasing dissolved alumina content. These partially conflicting factors led the German investigators to leach the clay semibatchwise in towers at 130°F and 9 atmospheres with about 17% dissolved sulfur dioxide. A maximum of 80% of the alumina was extracted under these conditions in 15 hours to produce a liquor containing a maximum of 60 gpl soluble alumina.

The German engineers chose these leaching conditions after very intensive investigation of the leaching process. It is still possible that some form of more efficient leaching process could be developed, but this would take a great deal of effort and, even if successful, would not yield a decisive cost reduction. Otherwise, no way is known of improving upon the German approach. The leach can be accomplished as described but will be costly. Inevitable leaks of sulfur dioxide from the pressurized system will cause environmental problems that were ignored at the time the previous work was done but which would be very costly to solve today.

4.4.3.5 Blowdown

Slurry at the completion of leaching is passed into a blowdown tank for the purpose of removing excess SO_2 and reducing the pressure to atmospheric. The concentrated SO_2 evolved passes into the SO_2 recovery system from which it is eventually recompressed and returned to leaching.

Design of the blowdown tank presents no particular problems. It would be very desirable to utilize the pressure existing in the leach tank to effect an initial separation of waste solids in the presence of a high partial pressure of SO_2 by means of a pressurized filtration. This is not known to be practical--in part because of the difficulty of bringing the filtered solids out of the pressurized zone in the presence of SO_2. It might be possible to utilize the leach tank pressure to obtain a sand separation in a hydrocyclone of special design, but development work would be required due to the evolution of gas as the pressure is decreased.

4.4.3.6 Solid-Liquid Separation

German practice reportedly involved the use of a very large area of leaf filters, with washing in the filter. This would be a very costly operation today. Vacuum filtration is not applicable, because the consequent reduction in pressure would cause further SO_2 evolution and precipitation of alumina. Any contemplated application of sulfurous acid leaching today would almost surely involve an effort to develop a countercurrent decantation system for solid-liquid separation. This would probably be difficult in view of the known reactivity of the silica and the semicolloidal nature of at least a part of it. Unfortunately, the German reports give very little specific information on the properties of the silica residue.

4.4.3.7 Tailings Disposal

The residue from leaching, although consisting primarily of a reactive silica, is considered to have no value. It is pumped to disposal, probably in a mined out clay pit. If an analysis of the tailings approximating that given in USBM RI 5997 can be attained, no special precautions would be necessary to insure isolation of tailings drainage water from the environment. Nothing is known about the suitability of sulfurous acid leach residue as subsoil.

4.4.3.8 First Autoclaving

The purpose of the first autoclaving of the primary liquor stream is to decompose under carefully controlled conditions the dissolved aluminum sulfite so as to produce an insoluble basic aluminum sulfite crystalline in form, and therefore filterable. The overall reaction is:

$$\underset{\text{solution}}{Al_2(SO_3)_3} + 6H_2O \longrightarrow \underset{\text{semicrystalline precipitate}}{\left[2(AlOHSO_3)\right]\cdot 5H_2O} + SO_2\uparrow$$

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The combined leach liquor and washings from waste solid separation is pumped into heat exchangers where it is heated to 212°F with heat recovered from acid vapor streams exiting both sets of autoclaves and the thickener overflow from the first autoclaving. The hot liquor is autoclaved for 2 hrs @ 212°F under three atmospheres SO_2 pressure with the direct addition of live steam to precipitate aluminum monobasic sulfite. Sulfur dioxide is evolved and passes to recovery.

The aluminum monobasic sulfite is reportedly crystalline and can be settled or filtered reasonably well although no quantitative data are available. It is thickened in the absence of air, with approximately 55% of the solution as overflow returning to leaching.

4.4.3.9 Second Autoclaving

A choice is possible at this point in the process between filtration and washing of the thickener underflow from the preceding step followed by mild calcination to produce a modified Bayer process feed, or a second autoclaving to decompose hydrothermally the basic sulfite produced in the first step. Fulda-Ginsberg reports that development of the hydrothermal decomposition, in which the trihydrate produced retains the crystal structure of the basic sulfite, was considered to be an important technical advance.

The overall reaction is:

$$\underset{\text{Semicrystalline precipitate}}{AlOHSO_3} + H_2O \longrightarrow \underset{\text{Semicrystalline precipitate}}{Al(OH)_3} + \underset{\text{Gas}}{SO_2} \uparrow$$

The thickener underflow from the preceding step is pumped first to heat exchangers and then into the second autoclave. This autoclave is maintained at 310°F and 7 atmospheres, primarily steam pressure, for at least 10 minutes by means of indirect steam heating. A mixture of SO_2 and steam boils off which, after some heat recovery, goes to the acid regeneration system.

The precipitation of alumina trihydrate in the second autoclaving as reported by the German investigators appears technically feasible, but no mention is made in Fulda-Ginsberg of difficulties probably encountered. Scaling of metallic surfaces is to be expected, and apparently the trihydrate readily adsorbed impurity metal hydroxides.

4.4.3.10 Filtration and Washing

The residual slurry is thickened, filtered, and washed to yield a crude trihydrate. The mother liquor is boiled at atmospheric pressure to recover some additional SO_2 and is then discharged to waste. No information is available, but it is probable that this mother liquor contains sufficient dissolved materials--sulfur in a multiplicity of valence states in particular--to render it unacceptable for return to leaching, for use as acid absorber water, or as a discharge to the environment. An R&D effort will be required to determine what disposition can be made of this 13 mass units of liquor per mass unit of alumina product.

4.4.3.11 Technical Evaluation of Preceding Steps

The German effort to utilize sulfurous acid in the manufacture of alumina from clay is the only known reported actual experience with this acid and therefore is the only basis for technical evaluation of the foregoing steps. All of the steps appear reasonable although very little of the quantitative information that would be required for an engineering design of the process has been reported. It is concluded that the process could be operated as described but that the thermal energy requirements--with the possible exception of the clay calcination step--would be approximately the same as reported in German practice. Some improvement in crude alumina trihydrate product quality would probably be obtained from the use as raw material of U.S. kaolin, which is of a better quality than the German clay. The Germans did intensive research on the basic process to bring it to the present state of development. The prospects for any major cost reductions or producing without alkaline refining alumina meeting reduction grade specifications are virtually nil. Environmental protection, which was of little or no concern in wartime Germany, would be a major problem today.

4.4.3.12 Acid Recovery System

Makeup sulfurous acid is provided by burning sulfur with air and then absorbing the SO_2 into water at 3 atmospheres. Approximately 11.4 mass units water/mass unit alumina are required for this absorption. This water is rejected from the process as waste liquor from the settling-filtration following the second autoclaving; but if present day environmental considerations required treatment of this waste liquor involving evaporation, a substantial additional process energy requirement for evaporation would result, because the amount of absorber water cannot easily be reduced.

Sulfurous acid produced at 3 atmospheres is pumped into a second absorber operating at 9 atmospheres in which it is combined with various recycle streams to prepare the leach acid.

Sulfur consumption is as high as approximately 20% on product alumina. An unknown fraction of the sulfur loss must be due to leakage from the pressurized system although it is very much to the German design engineers' credit that they succeeded in designing an almost totally closed system.

Another fraction of the sulfur loss is due to oxidation of SO_2 to SO_4 in solution. Sulfur is multivalent. Some of the required oxygen undoubtedly comes from air, but it is known that a large part of it comes from the reduction of SO_2 to elemental S. Sulfur compounds of other valences also formed to an unknown extent.

An operable acid recovery system incorporating provision for adding makeup can be designed on the basis of presently available information. Unfortunately there is no known solution to the problem of sulfur disproportionation in the process, which is a major cause of sulfur consumption and which also interferes in the modified Bayer refinement as discussed below.

4.4.3.13 Modified Bayer Refining Process

The German investigators were never able to produce an alumina of reduction grade quality from the sulfurous acid process directly. Alumina trihydrate produced in the second autoclaving was therefore refined in a modified Bayer process. The removal of iron originally in the clay was deliberately avoided in order to facilitate the removal of titanium, chromium and vanadium by coprecipitation with iron in the Bayer treatment.

The alumina trihydrate from the second autoclaving was an exceptional Bayer process feed, reportedly going readily into solution in caustic soda at one atmosphere and 140°-175°F with warming of the liquor from the heat of solution to 195°-200°F. The German feed contained approximately 10% Fe_2O_3 and 0.5% SiO_2, but feed prepared from lower iron content U.S. kaolin would undoubtedly contain substantially less iron. Not discussed in terms of its effect on the Bayer refining was 2-2.5% elemental sulfur produced by disproportionation. This sulfur is very finely divided and would be expected to dissolve in the Bayer process liquor. Special measures would be necessary for its control in a cyclic process. On the other hand, sulfite refined feed derived from calcined kaolin would contain no organics, which would tend to simplify the caustic purification step.

The technology of the caustic purification step, with the exception of dealing with a feed containing reactive elemental sulfur in the amount indicated, is well known; and a demonstration plant can be designed without additional pilot work. It is expected that demonstration plant design information required for sulfur control can be developed from bench-scale studies.

4.4.4 Alumina Product Quality

There appears to be no hope, based upon intensive German research, for producing alumina meeting reduction grade specifications without caustic purification. There appears to be no doubt that sulfurous acid extracted alumina which has been subjected to caustic purification will meet the chemical and physical properties specifications for reduction grade alumina, and that such alumina will be interchangeable with Bayer alumina produced from bauxite.

4.4.5 Energy Requirements

The net energy requirements to process are summarized as follows:

	Btu/ton Al_2O_3
Clay calcination	6.7×10^6
Autoclaving	14.0×10^6
Caustic Purification	3.6×10^6
Product Alumina Calcination	3.9×10^6
	28.2×10^6

Coal may be used for clay calcination and for the generation of steam. The final product alumina calcination, assuming that present day Bayer process technology is used, will require a high grade fuel which will not compromise the product alumina quality.

The energy requirements for the overall process are high, because the clay requires calcination, the maximum soluble alumina loading which is possible in the leach liquor is low, the hydrolysis of the intermediate aluminum salt is carried out in two stages, and the primary product alumina is put into solution twice during the processing sequence. It is possible that the heat requirement for clay calcination, as discussed elsewhere, may be reduced by the employment of fluidized solids calcination. The requirement for steam may probably be reduced a substantial but presently unknown amount by extensive and innovative heat recovery design. On the other hand, approximately 13 mass units of waste liquor/unit product alumina are now planned to be discharged to the environment. If this discharge cannot be accomplished under today's environmental protection standards without resort to a fuel-fired evaporative process, a very substantial process energy requirement will be added to the total.

4.4.6 Environmental Protection

Waste solids are expected to be disposed of in exhausted clay pits. The properties of the solids as subsoil are not known, but the water accompanying the waste solids is not expected to present any particular problem. Iron and minor constituent metal oxides will be discharged from the caustic purification section as a red mud similar to Bayer process red mud but in much smaller quantities. This mud will require impoundment in a manner similar to bauxitic Bayer process red mud. The nature and disposition of caustic purification sulfur-bearing residues is unknown. The treatment required and disposition of waste process liquor (as discussed in preceding sections) is unknown.

The absorption of SO_2 into water is very difficult in the presence of inerts. This process has been carefully designed as a totally closed system so as to avoid, this problem. Leaks from the pressurized processing system may however, cause environmental problems.

4. 4. 7 General Comments

(1) Pressurized acid preparation, digestion, and two stages of thermal hydrolysis are required.

(2) A relatively long period of time is required for the digestion of calcined clay with sulfurous acid, even under pressure, and even then only about 80% of the alumina is extracted.

(3) Air must be rigorously excluded from digestion, the two stages of thermal hydrolysis and the thickening/filtration operations associated with thermal hydrolysis in order to minimize the oxidation of sulfite to sulfate. Even with exclusion of air, sulfate, elemental sulfur and sulfur compounds of other valence states are formed which together with other losses impose a makeup sulfur requirement of up to approximately 20% by weight on alumina. Any original advantage of inexpensive acid is lost by conversion of the SO_2 to nonrecyclable forms.

(4) The process has very little ability to separate alumina from impurity metal oxides in the entering clay, and silica is not rejected adequately. Even after intensive study, a caustic purification (modified Bayer) process appears to be required in order to manufacture alumina meeting reduction grade specifications. Alumina so prepared should be of excellent quality and interchangeable with Bayer alumina produced from bauxite.

(5) Energy requirements are high despite the relatively low heat of formation of aluminum sulfite from the oxides because of the low solubility of alumina in the leach liquor, the employment of a two-stage thermal hydrolysis, and the requirement that the primary product alumina stream be put into solution twice. The energy requirement will be substantially increased if it is found, as is probable, that approximately 50% of the leach liquor, which in wartime Germany was apparently simply discharged to the environment, must be subjected to evaporation. A substantial amount of electrical or other equivalent energy is required for gas compression.

(6) The low alumina loading achievable in process liquors will influence both capital and operating costs.

(7) The relatively easy hydrothermal decomposition of the intermediate aluminum sulfite is a distinct process advantage.

(8) Air and water environmental control problems, of little or no concern at the time of the major thrust of process development, would be difficult and costly to solve so as to meet today's standards.

(9) The process has already been studied so extensively that the prospect of a major cost-reducing breakthrough is very small.

4.4.8 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000 ton/d of alumina.

(2) The chemical analysis of the clay feed (dry basis) is as follows:

Al_2O_3	36.5%
Fe_2O_3	0.86
SiO_2	46.4
L. O. I. *	13.54
Other*	2.7
Total	100.00%

*Other is primarily TiO_2.

(3) The raw clay feed to the process contains 18.5% free moisture.

(4) A rotary kiln is used for the dehydration of the clay feedstock.

(5) There is a 1% dust loss (calcined basis) from the dehydration rotary kilns.

(6) 80% extraction efficiency of Al_2O_3 is achieved in the SO_2 leaching step.

(7) 75% of other metal impurities is solubilized in the leaching step.

(8) 81.25% of Fe_2O_3 is solubilized in the leaching step.

(9) 0.3% of SiO_2 is solubilized in the leaching step.

(10) The waste leach mud after filtration will contain 30% moisture.

(11) One-half of the liquor into the thickener following the first autoclaving step (precipitation of monobasic aluminum sulfite) will exit via overflow and one-half will exit with underflow solids (equivalent to approximately 20% solids in the underflow).

(12) The decomposition of monobasic aluminum sulfite to alumina will be accomplished at a 97% efficiency (7 atm autoclaving).

(13) The product stream from the monobasic aluminum sulfite decomposition is used to preheat the feed to this process step.

(14) Approximately 9% of contained SO_2 is lost as sulfur and sulfate during the monobasic aluminum sulfite decomposition.

(15) Crude alumina product from filtration will contain approximately 42% free and combined water.

(16) In the acid recovery section, sulfur is burned with air to produce a stoichiometric amount of SO_2 for makeup.

(17) There is a 2-ton/d SO_2 loss from the 3 atm absorber in the acid recovery system.

(18) Waste heat is recovered from the sulfur burner.

(19) There is a 100% absorption efficiency of acid vapors in the 9 atm absorber in the acid recovery system.

(20) The purification of crude alumina product is accomplished by leaching with caustic in a modified Bayer plant.

(21) Sulfur and Fe_2O_3 compounds precipitate during caustic digestion and are removed with the red mud waste solids.

(22) The filtered and washed red mud will contain 55% moisture.

(23) No conversion of NaOH to Na_2CO_3 is considered.

(24) Approximately half of the alumina precipitates while the balance is recycled.

(25) Caustic concentration during digestion is approximately 9.5% by weight as NaOH.

(26) A 5-effect evaporator is used to concentrate the recycle caustic liquor stream.

(27) The trihydrate alumina feed to calcination will contain approximately 11% free moisture.

(28) A rotary kiln is used to calcine the alumina product.

(29) There is a 1% dust loss (calcined basis) from the rotary kiln calcination of alumina.

(30) The over-all recovery of alumina in the caustic purification section is approximately 95%.

TABLE 4-4-1

ALUMINA FROM CLAY
SULFUROUS ACID PROCESS
DAILY THERMAL REQUIREMENTS
FOR 1,000 TON/D·Al_2O_3

	250 LB/IN^2 (GA) STEAM, M LBS (830 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
CLAY PREPARATION			
CALCINATION	–	6,655	–
CRUDE ALUMINA PRODUCTION			
LEACHING	–	–	931
1st AUTOCLAVES (PRECIPITATION)	506*	–	–
2nd AUTOCLAVES (DECOMPOSITION)	16,484	–	–
ACID RECOVERY			
SULFUR BURNER	(132)**	–	531
COMPRESSION	–	–	307
RECYCLE GASES	–	–	19,588
CAUSTIC PURIFICATION			
DIGESTION	3,596	–	–
PRECIPITATION	–	–	10,326
CALCINATION	–	3,907	–
EVAPORATION (5-effect)	744	–	1,460
TOTALS	**21,198** **(17,594 MM BTU)**	**10,562**	**33,143**

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 28,156 MM BTU/D *OR* 28.2 MM BTU/TON Al_2O_3

* Heat equivalent to an additional 8,688 M lbs of 250 lb/in^2 (ga) steam is recovered from recycle streams for heating autoclave feed.

** Steam credit from waste heat boiler.

Table 4-4-2 (Sheet 1 of 4)

Alumina from Clay/Sulfurous Acid Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	1	2	3	4	5	6	7	8	9	10	11	12
Component												
Al_2O_3	1364	1364	14	1350	1350	1382		1382		270	1112	
Fe_2O_3	32	32		32	32	58		58		6	52	
NaOH												
SiO_2	1734	1734	18	1716	1716	1716		1716		1711	5	
Other	101	101	1	100	100	175		175		25	150	
L.O.I.	506	506	506									
H_2O	843	843	843			28599	114	28485	1726	863	29348	253
S												
SO_2						5697	2265	3432		1	3431	
SO_3												
O_2												
Total	4580	4580	1382	3198	3198	37627	2379	35248	1726	2876	34098	253

All units are in short tons per day.

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Table 4-4-2 (Sheet 2 of 4)

Alumina from Clay/Sulfurous Acid Process Material Balance

Process Stream	13	14	15	16	17	18	19	20	21	22	23	24
Component												
Al_2O_3		1112	32	1080		1080		31	1049		2059	
Fe_2O_3		52	26	26		26		2	24		24	
NaOH										10	2879	
SiO_2		5		5		5			5		5	
Other		150	75	75		75		72	3		3	
L.O.I.												
H_2O	125	29476	14738	14738	2991	11747	800	11747	800	10	25458	235
S									22		22	
SO_2	1330	2101	488	1613	1358	255		121				
SO_3								112				
O_2												
Total	1455	32896	15359	17537	4349	13188	800	12085	1903	20	30450	235

Table 4-4-2 (Sheet 3 of 4)

Alumina from Clay/Sulfurous Acid Process Material Balance

Process Stream	25	26	27	28	29	30	31	32	33	34	35	36
Component												
Al_2O_3	39	2020	2558	1504	1054		44	1010	10	1000	538	1010
Fe_2O_3	24											
NaOH	4	2875	2968	2843	125		119	6		6	93	2869
SiO_2	5											
Other		3	3		3			3		3		
L.O.I.												
H_2O	115	25578	26665	25031	1634	1010	1921	723	723		1087	25865
S	22											
SO_2												
SO_3												
O_2												
Total	209	30476	32194	29378	2816	1010	2084	1742	733	1009	1718	29744

Table 4-4-2 (Sheet 4 of 4)

Alumina from Clay/Sulfurous Acid Process Material Balance

Process Stream	37	38	39	40	41	42	43	44	45			
Component												
Al_2O_3		1010							32			
Fe_2O_3									26			
NaOH		2869										
SiO_2												
Other									75			
L.O.I.												
H_2O	1217	24648					10631	10631	28599			
S			129									
SO_2					2	258		256	5697			
SO_3												
O_2				129								
Total	1217	28527	129	129	2	258	10631	10887	34429			

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4.4.9 Equipment List

ALUMINA FROM SULFUROUS ACID/CLAY PROCESS

Clay Preparation Area

Belt conveyor, under wobbler feeder and primary crusher
Truck dump hopper
Wobbler feeder and hoppers from truck dump
Primary crusher and chutes
Belt conveyor, primary crushers to stockpile
Belt conveyor and distributors for stockpile
Stockpile, enclosure, dust collection system and reclaim system
Wobbler feeder from stockpile
Belt conveyor stockpile to hammermills
Hammermills and hoppers
Belt conveyor hammermills to elevator
Bucket elevators from secondary crusher
Vibrating screens, chutes and covers
Roll compactors with covers
Belt conveyor compactors to elevators
Belt conveyor screens to raw clay surge bin
Raw clay surge bin
Weigh belt feeders
Belt conveyors - raw clay surge bin to kiln
Rotary kilns
Apron feeders with covers from coolers
Calcine bucket elevators
Calcine vibrating screens and chutes
Calcine cage mill grinder with covers
Calcine apron feeder with cover
Bucket elevator to calcine storage bins
Calcine storage bins
Weigh belt feeders to leaching
Belt conveyors to leach tanks
Dust collection systems

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EQUIPMENT LIST (Cont)

Digestion, SO_2 Blowdown Area

Pug mill mixers
Leach head tanks
Leach slurry pumps
Leach vessels
Leach vessel agitators
Leach slurry transfer pumps
Leach blowdown tanks
Blowdown tank pumps

Slurry Filtration, 1st Autoclaving, Slurry Thickening, 2nd Autoclaving, Heat Interchange Area

Filter feed surge tank (lined)
Filter feed surge pumps
Pressure filters
Pressure filter slurry pit
Slurry pit agitator
Slurry pit sump pumps
Filtrate storage tanks (lined)
Filtrate pumps
Heat interchange system
Heat interchange pumps
Condensate pumps
Hotwell sump (lined)
Hotwell sump pump
Filtrate booster pumps
L. P. autoclaves
L. P. autoclaves transfer pumps
Slurry thickeners
Thickener transfer pumps
Thickener overflow pumps
H. P. autoclaves
H. P. autoclaves transfer pumps
H. P. autoclaves agitators
H. P. autoclaves product pumps
Fumes collection system

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EQUIPMENT LIST (Cont)

Pregnant Liquor Thickening, Filtration Area

Pregnant liquor thickeners (lined)
Pregnant liquor thickeners underflow pumps
Pregnant liquor thickeners overflow pumps
Crude alumina vacuum filtration system
Wet crude alumina conveyors
Wet crude alumina surge tanks

Sulfurous Acid Generation and Recovery Area

Sulfur unloading pumps
Sulfur storage tank with steam coils
Sulfur burner feed pumps
Sulfur burner system
Waste heat recovery boiler
L.P. absorber
Process water pumps
L.P. absorber underflow pumps
SO_2 gas compressors and coolers
H.P. autoclave SO_2 gas partial condenser
Partial condenser underflow pumps
H.P. absorber
H.P. absorber underflow pumps

Digestion, Filtration, Heat Interchange Area (Modified Bayer Process)

Crude alumina distribution conveyor with hoppers
Pug mill mixers
Crude alumina weigh feeders
Slurry head tanks
Digester feed pumps
Digesters
Digester agitators
Digester transfer pumps
Sodium aluminate slurry pumps

EQUIPMENT LIST (Cont)

Filter feed tank
Filter feed pumps
Vertical pressure filters
Slurry tanks
Slurry tank agitators
Filter slurry pumps
Filtrate storage tank
Filtrate transfer pumps
Caustic stream heat interchange system

Precipitation, Thickening Area (Modified Bayer Process)

Precipitation fill tanks
Precipitation fill pumps
Precipitators
Precipitator agitators and air lifts
Mid-stage flash tanks
Flash tank transfer pumps
Primary feed tank with baffles
Primary feed tank agitator
Primary feed pumps
Primary thickeners
Primary underflow pumps
Secondary thickeners
Secondary underflow pumps
Tertiary thickeners
Tertiary underflow pumps
Tertiary thickener rakes
Tertiary thickener overflow pumps
Primary wash tanks
Primary wash tank inlet screens
Primary wash pumps (hydrate slurry)
Secondary thickener surge tank
Secondary thickener surge tank agitators
Secondary thickener surge pumps
Tertiary thickener seed storage tank
Tertiary thickener seed pumps
Wash liquor tank
Wash liquor pumps

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EQUIPMENT LIST (Cont)

Evaporation, Calcination Area (Modified Bayer Process)

5-effect evaporator system
Evaporation test tank
Evaporator feed pumps
Digestion test tank
Digestion spent liquor pumps
Hydrate storage tanks
Slurry density tank
Slurry density tank agitators
Slurry density tank pumps
Hydrate filters
Filtrate receiver
Wash water receiver
Hydrate filter vacuum pumps
Filtrate pumps
Wash water pumps
Rotary calciners
Rotary coolers
Fluo-solids coolers
Cyclone dust collectors
Electrostatic precipitator
Alumina conveyors
Alumina storage silo

Auxiliary Tankage and Equipment Area (Modified Bayer Process)

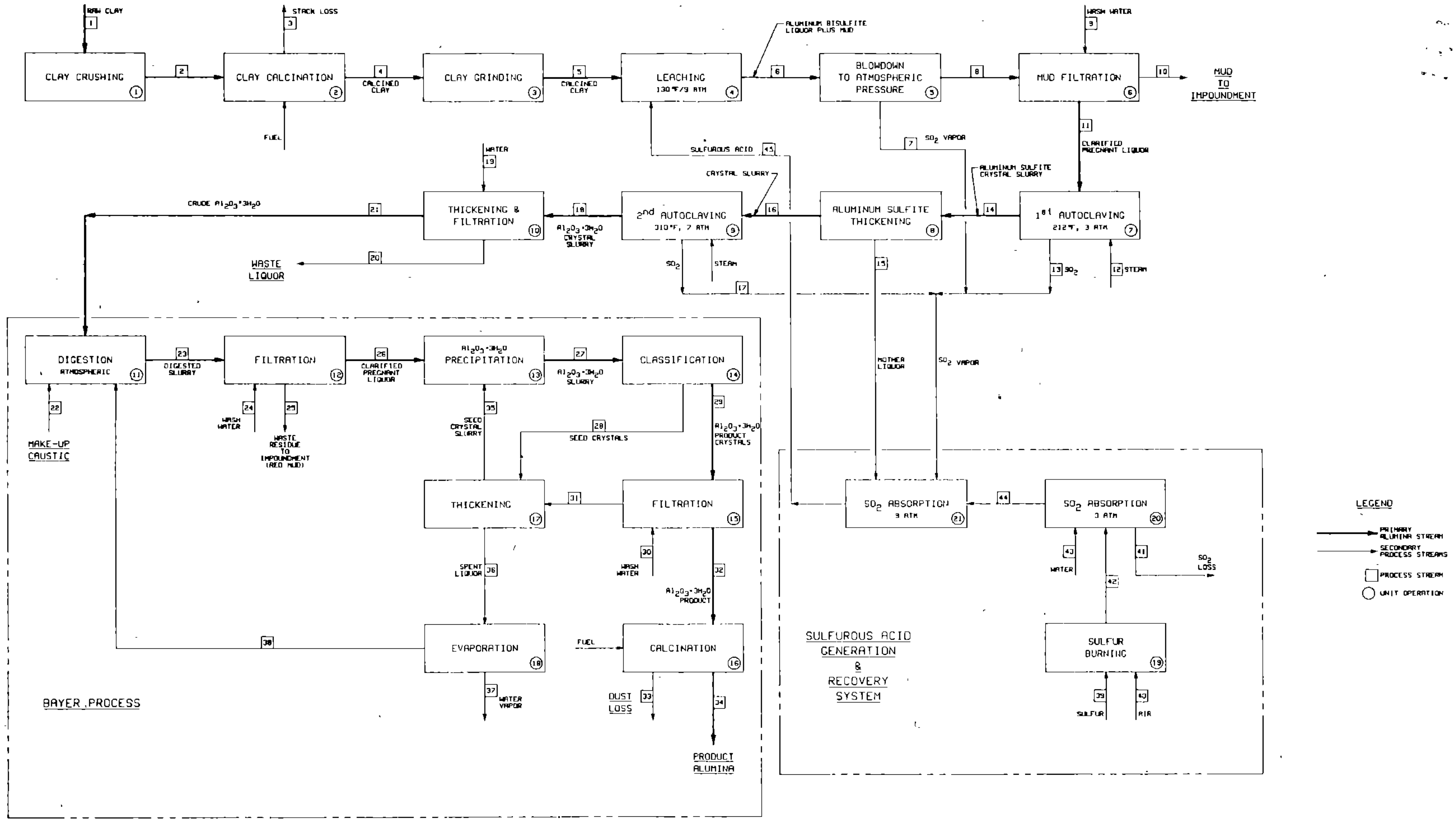
Caustic storage tank
Caustic transfer pumps
Dilute caustic tank
Dilute caustic pumps
Sump relay tank
Sump relay pumps
Sulfuric acid tank
Sulfuric acid pumps
Dilute sulfuric acid tank
Dilute sulfuric acid pumps
Sulfuric acid neutralization tank

EQUIPMENT LIST (Cont)

Sulfuric acid neutralization pumps
Condensate storage tank
Condensate pumps

Utilities

Steam plant and auxiliary systems
Cooling towers and auxiliary systems



NO	DATE	REVISION	BY	APP	APP.

NOTES

FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-4-2

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-4-1

DESCRIPTION COST ACCOUNT

CONSTRUCTION APPROVAL

APPROVAL DATE SCALE DATE

DESIGNED BY

DRAWN BY ADS

CHECKED BY

APPROVED BY

APPROVED BY

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO [illegible]

ALUMINA FROM CLAY

SULFUROUS ACID PROCESS

JOB No. 76161-001

FIGURE NO. 4-4-2

REVISION R.0

NOT REPRODUCIBLE

4.5 TECHNICAL APPRAISAL: ALUMINA FROM ANORTHOSITE VIA LIME SINTER PROCESS

4.5.1 Summary and Conclusions

The process being evaluated is one for the manufacture of reduction-grade alumina from anorthosite via a lime sinter process.

The anorthosite/lime sinter process includes the following steps:

(1) Preparation of sinter feed. This series of preparation steps includes crushing, grinding, separation, partial drying, and pelletizing which must be performed prior to the sintering of the anorthosite/limestone feed.

(2) Sintering of the anorthosite/limestone feed. This step also includes the "soaking" of the sintered pellets to permit "dusting" and subsequent separation of the "dusted" and "undusted" sinter.

(3) Leaching of the "dusted" sinter with spent soda ash liquor to solubilize the alumina values.

(4) Separation, washing, and rejection to disposal of the insoluble residue from the leaching step.

(5) DSP seeded desilication of the pregnant liquor and removal of DSP for seed recycle and bleed to the sinter kiln.

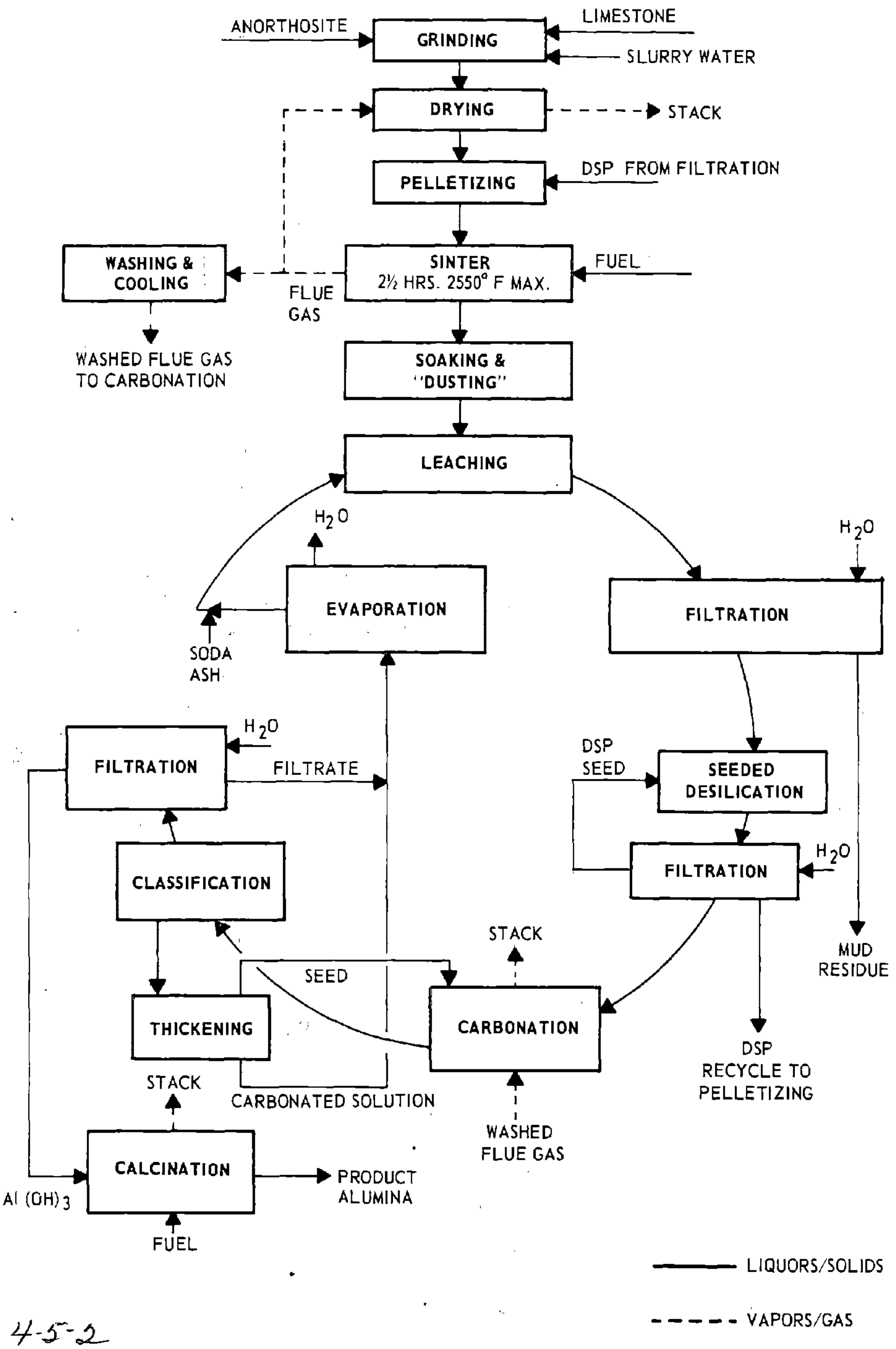
(6) Seeded carbonation of the desilicated pregnant liquor with washed flue gas from the sintering kilns. This precipitates the alumina as the trihydrate which is classified into a fine fraction for seed recycle and a coarse fraction for filtration and further processing.

(7) Alumina trihydrate from filtration is calcined to product alumina.

(8) The spent soda ash liquor from the filtration of the alumina trihydrate and seed preparation is concentrated by evaporation and recycled with makeup soda ash to the leaching step.

FIGURE 4-5-1

ALUMINA FROM ANORTHOSITE VIA LIME SINTER



(9) The flue gas from the sintering kilns is washed and a portion compressed for use in the carbonation step.

The process being evaluated has been constructed from information derived from U.S. Bureau of Mines Reports of Investigations, information published in the open literature, and Kaiser Aluminum experience.

The quality of alumina produced in this process should be equivalent to that produced in a Bayer plant. Further study may be required to characterize particular anorthosite ore bodies for minor impurities and to determine their effect on process impurity removal requirements.

The estimated thermal energy requirement for this process is 61.9×10^6 Btu/ton Al_2O_3. It is very high even though it utilizes waste heat from the sinter kiln flue gases for all steam and drying requirements. This high energy requirement is due to the 58×10^6 Btu/ton Al_2O_3 estimated for the sintering step of this process. This large energy consuming step alone is almost prohibitive.

Gelation in the leaching section is potentially the most serious technical problem of this process. Although investigations indicate that gelation can be prevented by careful control of the sintering and leaching operations, the possibility that gelation may occur is a serious disadvantage of this process.

Disposal of the waste leach residue is also a serious problem in this process due to its sheer quantity. The waste solids which must be disposed of approaches 2/3 of the total plant feed or approximately 10 tons per ton of alumina produced.

The recovery of alumina in the leach process is only 75% which constitutes another penalty incurred by this process.

4.5.2 Background

Development of a lime-soda sinter process began as long ago as 1902 when Adolf Kayser obtained a patent on a process for separating alumina from silica. Early work on lime-soda sinter processes was reviewed by Conley and Edwards, Frary, and Jeffries.

Conley investigated the extraction of alumina from Pennsylvania nodular diaspore clay by a lime-soda sinter process. In this process clay was dry ground and then sintered with limestone and soda ash (sodium carbonate) to convert the alumina to sodium aluminate and the silica to dicalcium silicate. The sinter was leached with sodium carbonate solution to dissolve the sodium aluminate. The solution was then heated under pressure with lime to remove most of the silica that dissolved with the sodium aluminate. The purified solution was carbonated to precipitate alumina trihydrate which was then calcined to produce alumina.

During World War II the Defense Plant Corporation financed the construction of a 50-ton-a-day plant at Laramie, Wyoming, to produce alumina from anorthosite. Construction of this plant was almost completed when the program was terminated in 1945. In 1952 the Bureau of Mines modified the plant and operated it on an experimental basis. Operation of this plant was described in Bureau of Mines Bulletin 577. In this process crushed anorthosite and limestone were mixed and ground in a recycled soda solution in a ball mill. The wet mix was sintered and then wet ground with soda solution in a ball mill which served as the first leaching stage. The remaining process steps were similar to those used in the process treating Pennsylvania diaspore clay. The solution was heated under pressure with lime and then carbonated to precipitate alumina trihydrate.

The process evaluated herein is somewhat different than any of the previous studies in that it is an anorthosite/limestone sinter with no addition of soda to the sintering step. It cannot however be considered a true lime-sinter process, because the soda content of the anorthosite used in this study is equivalent to about 20 percent of the quantity required in the lime-soda sinter process. It therefore falls somewhere in between these processes. Information contained in Bureau of Mines RI7068 was used extensively in developing this process.

4.5.3 The Process

4.5.3.1 Summary

Anorthosite and limestone are crushed in separate circuits and then ground and blended in a wet milling step. The ground slurry is classified and the minus 200 mesh fraction is thickened, filtered and partially dried. The resultant 12 percent moisture ground rock blend is then mixed with desilication product (DSP) filter cake from the desilication step and pelletized. The pellets are fed to sintering kilns and reacted at 2550°F to produce mainly calcium aluminates and calcium silicates. The sintered product is cooled to 1290°F and then soaked at that temperature to allow for the formation of β-dicalcium silicate. Rapid cooling to 77°F then "dusts" the sinter by transforming β-dicalcium silicate to the γ-form which expands its volume by approximately 10 percent. The "dusted" sinter is screened to achieve separation of the "undusted" portion which is recycled to the sinter kilns.

The "dusted" sinter is leached at 140°F with a spent solution of soda ash thereby extracting the alumina as sodium aluminate and precipitating calcium carbonate. The insoluble residue is separated by filtration and discarded. The pregnant liquor, including the washings, is desilicated at 212°F by seeding with DSP. The desilicated solution is then filtered. Most of the DSP is recycled as seed, but a bleed of DSP is sent to pelletizing and reprocessed through the sintering kilns.

Desilicated pregnant liquor is carbonated with washed sinter kiln gases in the presence of alumina trihydrate seed, thereby precipitating alumina trihydrate. The coarse alumina trihydrate is separated by classification with the fine fraction being thickened and recycled as seed to carbonation. The coarse alumina trihydrate is filtered and fed to kilns where it is converted to alumina. The spent liquor from the filtration and thickening operations is concentrated by evaporation and makeup soda ash added before its recycling to the leaching step.

4.5.3.2 Preparation of Sinter Feed

This series of preparation steps includes crushing, wet grinding, wet classification, separation, partial drying, and pelletizing to produce an intimate blend of 98 percent minus 200 mesh anorthosite and limestone for sinter feed. The crushing section, consisting of jaw and cone crushers, prepares the anorthosite and limestone for subsequent wet grinding in ball or rod mills. The mill overflow is classified in a hydroseparator or wet cyclones with recycle of the coarse fraction to wet milling. The minus 200 mesh rock slurry is thickened with the aid of flocculant and dewatered using vacuum filters to a 17 percent moisture cake.

The filter cake is partially dried in a rotary dryer which utilizes waste heat from the sinter kiln flue gases. The partially dried ground rock solids at 12 percent moisture are then pelletized to yield an intimate blend of anorthosite and limestone in the form of 1/8 inch by 1/4 inch diameter balls. A bleed stream of DSP from the desilication of pregnant liquor is also pelletized with the ground rock slurry.

This preparation section is very important to the overall process as it must produce an intimate blend of anorthosite and limestone in the correct ratio so that it will react properly in the sintering kilns. A good sinter will, in turn, leach and process without gelation and yield a high alumina extraction. The control in the preparation section must be very precise to achieve this goal.

Pelletizing of the raw material mixture will require further investigation to determine the optimum pellet characteristics.

4.5.3.3 Sintering Operations

The pellets of anorthosite/limestone are fed to sintering kilns where they are heated to a maximum temperature of 2550°F. During a total retention of 2 1/2 hrs, the alumina and silica react with the limestone. The main reactions are represented as follows:

anorthite

$$7(CaO\cdot Al_2O_3\cdot 2SiO_2) + 33CaCO_3 \longrightarrow 12CaO\cdot 7Al_2O_3 + 14(2CaO\cdot SiO_2) + 33CO_2$$

albite

$$(Na_2O\cdot Al_2O_3\cdot 6SiO_2) + 12CaCO_3 \longrightarrow 2NaAlO_2 + 6(2CaO\cdot SiO_2) + 12CO_2$$

Excessive sintering temperatures and/or sintering times produce gehlenite ($2CaO\cdot Al_2O_3\cdot SiO_2$). Alumina is not recoverable by leaching gehlenite. Excessive $CaCO_3$ in the sinter mix forms tricalcium silicate ($3CaO\cdot SiO_2$), one of the portland cement products which causes gelation during the leaching step.

Maximum alumina extraction requires maximum formation of $12CaO \cdot 7Al_2O_3$ with a minimum excess of $CaCO_3$. A very careful stoichiometric balance must therefore be obtained in mixing anorthosite and limestone for the sinter to achieve this maximum extraction and to avoid subsequent gelation.

The sintered product from the kilns is cooled in rotary coolers to a temperature of 1290°F.

4.5.3.4 Soaking and "Dusting"

The sintering step produces dicalcium silicate. Soaking in a rotary calciner at 1290°F for 15 to 30 minutes allows the α-form of dicalcium silicate to convert to the β-form. When the β-form is subsequently cooled rapidly to 77°F in another cooler, it converts to the γ-form with a 10 percent increase in volume which results in the disintegration of the sinter and the formation of "dust". The following equations represent these reactions:

$$\alpha 2CaO \cdot SiO_2 \xrightarrow{1247\text{-}1301^\circ F} \beta 2CaO \cdot SiO_2$$

$$\beta 2CaO \cdot SiO_2 \xrightarrow{572\text{-}752^\circ F} \gamma 2CaO \cdot SiO_2$$

This operation is described in a patent by Kapolyi (Hung. Teljes 4240, April 1970).

There are several inhibitors noted for the above-desired conversion of β to γ dicalcium silicate which tend to stabilize the β form. They are carbon, $3CaO \cdot SiO_2$, and the higher oxides of Cr, As, Mn, Te, P, Ge, and V. Excess Na_2O is also mentioned as a stabilizer.

The theoretical yield would be for all the $2CaO \cdot SiO_2$ to form dust less than 325 mesh. In practice, about 95 percent "dusting" has been achieved in laboratory batch experiments. The "dusting" yield however has been quite variable and is greatly dependent on the proper ratio of anorthosite/limestone and sintering control. Without a good "dusting" yield, a prohibitive amount of coarse sinter would have to be recycled to the sinter kiln. Not enough information is currently available to indicate what happens to this recycle during resintering. If "dusting" yield is poor, the milling of sinter might become a requirement.

The "dusted" sinter is screened to remove plus 20 mesh particles which are recycled to the sinter kiln. The minus 20 mesh "dusted" sinter is conveyed to the leaching section.

4.5.3.5 Leaching

The dusted sinter is leached at 140°F for 30 minutes with a spent liquor solution from evaporation. The leaching solution will have a sodium carbonate concentration of approximately 170 g/l and a residual Al_2O_3 concentration of approximately 10 g/l. The slurry in the leach tanks will contain between 25-30% solids.

The main reaction during leaching is as follows:

$$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 + 5H_2O \rightarrow 14NaAlO_2 +$$

$$12CaCO_3 + 10NaOH$$

No flue gas (CO_2) is added to the leaching step in this process so as to allow for about 20 g/l free alkali (as NaOH) to hold the alumina in solution. The pregnant liquor will contain approximately 50 g/l Al_2O_3 and a total soda concentration of approximately 150 g/l expressed as Na_2CO_3. It will also contain about 1 g/l SiO_2 in solution. During the leaching operation, approximately 75 percent of the alumina in the anorthosite will be extracted.

Filters instead of thickeners are used to separate the insoluble residue from the pregnant liquor in order to avoid the problem of gelation. Literature and experience have shown that even when all precautions are taken to make a "good" sinter, gelation can still be a problem in anorthosite/limestone sinter processes. This process has been designed assuming that gelation will not occur. Gelation will however probably be the major operating problem in this process. The magnitude of this problem was shown during the Bureau of Mines experimental operation of the Laramie plant when operations had to be shut down to remove the solid mass with air hammers.

The filtered and washed leach residue consists of an enormous quantity of approximately 10 tons per ton of alumina which must be disposed of. This residue weight is approximately 2/3 of the feed to the process. These solids also contain entrained liquor which make them alkaline and therefore requiring care in disposing of them.

4.5.3.6 Desilication

DSP seeded desilication is utilized in this process. The pregnant liquor from leaching contains approximately 1 g/l SiO_2 in solution which must be removed before alumina is precipitated as the trihydrate. The pregnant liquor is desilicated by seeding with about 100 g/l DSP solids and holding in stirred tanks at 212°F for 24 hrs. The desilicated slurry is filtered to remove the DSP solids, most of which are recycled back to desilication as seed. A bleed quantity of DSP equal to that which is removed by desilicating is washed and recycled to the sinter kiln to reclaim its soda and alumina values. The desilicated pregnant liquor will contain about 0.035 g/l SiO_2.

Although data are not available on DSP seeded desilication for liquors of this composition, it is believed to be the best technology for this process.

4.5.3.7 Carbonation

The desilicated solution is carbonated to precipitate alumina trihydrate as shown in the following equation:

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow Al_2O_3 \cdot 3H_2O + Na_2CO_3$$

Precipitation of the alumina is aided by adding alumina trihydrate seed crystals equivalent to 25 percent of the alumina that precipitates.

The seed crystals are recycled fines from the classification of the precipitate. The carbon dioxide gas is obtained from the sinter kiln stack gases after they have been scrubbed and cooled.

The carbonators are operated at 140°F and the retention time is 12 hrs. Sufficient carbon dioxide is added to precipitate 85 percent of the alumina in solution. Under these conditions, approximately 1/3 of the silica present in the liquor will precipitate.

The coarse alumina trihydrate crystals are separated from the fine seed crystals by hydro-classification. The coarse crystals are dewatered and washed on vacuum filters and conveyed to the calcination kilns. The fine seed crystals that remain in the hydro separator overflow are settled in thickeners and recycled to the carbonators. The carbonated overflow solution from the thickeners is pumped to soda ash recovery.

4.5.3.8 Calcination

The coarse alumina trihydrate crystals are calcined at 2000°F in rotary kilns to form alumina product as shown in the following equation:

$$Al_2O_3 \cdot 3H_2O \longrightarrow Al_2O_3 + 3H_2O$$

The calcined alumina is conveyed to storage silos where it is held until shipped.

4.5.3.9 Soda Ash Recovery

The spent carbonated solutions are concentrated in multiple effect evaporators. Makeup soda ash is added as required to the concentrated solution from the evaporator and the solution is recycled to the leaching section of the process.

4.5.3.10 Flue Gas Processing

The carbon dioxide gas used to carbonate the desilicated pregnant liquor is obtained from the sintering kilns. The stack gas from the kilns contains carbon dioxide evolved from the decomposition of the limestone in the feed and from the combustion of the coal fuel. The dust is removed from the gas in cyclones and heat is recovered as 100 psig steam from waste heat boilers. After leaving the waste heat boilers, the gas is processed through Venturi scrubbers for washing and further cooling before use in carbonation or venting to the atmosphere.

4.5.4 Alumina Product Quality

The quality of alumina produced by this process should be equivalent to that produced in a Bayer plant. If the degree of carbonation is

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properly controlled, the silica content and the purity of alumina produced by carbonation should be equal to that produced by Bayer precipitation.

Considerable amounts of impurities may be introduced into the liquors dependent upon the analysis of the limestone, fuel, and anorthosite. Some form of impurity control may be required to remove them from the plant liquor. The effect of impurities other than silica and iron on the process are largely unknown.

4.5.5 Energy Requirements

The process energy requirements are summarized as follows:

	Btu/ton Al_2O_3
Sintering Operations	61.6×10^6
Leaching	2.6×10^6
Desilication	2.8×10^6
Evaporation	3.9×10^6
Alumina Calcination	3.9×10^6
Waste Heat Recovery from Sinter Kiln Gases	(12.9×10^6)
TOTAL	61.9×10^6

Coal may be used for anorthosite/limestone sintering. The final product alumina calcination will require high grade fuel which will not compromise the product alumina quality.

The overall energy requirement for the process is quite high even after utilizing waste heat from the sinter kiln flue gases for all the steam requirements and the partial drying step before sintering. This high energy requirement of 58.0×10^6 Btu/ton Al_2O_3 that is required for the sintering step alone is due to the very large mass of anorthosite/limestone feed (17.4 tons/ton of alumina produced). This large energy consuming step alone makes the operating costs of this process almost prohibitive and certainly noncompetitive with the other processes being studied.

4.5.6 Environmental Control

Because of the large quantity of waste leach residue generated by this anorthosite-lime sinter process, its disposal will be a serious problem. One method of discarding the waste solids would be the use of tailing ponds. However, the size of the ponds may be so large as to make this disposal method undesirable. It is estimated that the waste solids which must be disposed of will approach 2/3 of the total plant feed or approximately 10,000 tons/day on a dry basis. These solids will also contain some entrained liquor which will make them alkaline; therefore runoff from any impoundment area must be treated.

The sinter kilns will require good dust removal equipment which will probably include wet scrubbers. SO_2 removal may also be required depending on the quality of coal used in the sinter kilns. Scrubber liquors will require impoundment and probably treatment for pH control.

4.5.7 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000 ton/d of alumina.

(2) The chemical analysis of the anorthosite feed (dry basis) is as follows:

Al_2O_3	26.0%
Na_2O	4.0
K_2O	1.0
SiO_2	53.0
CaO	11.5
MgO	0.3
Fe_2O_3	2.0
CO_2	-
Other	2.2
TOTAL	100.0%

(3) The raw anorthosite feed to the process contains 2% free moisture.

(4) The chemical analysis of the limestone feed (dry basis) is as follows:

Al_2O_3	0.8 %
Na_2O	0.04
K_2O	0.12
SiO_2	1.4
CaO	54.0
MgO	0.2
Fe_2O_3	0.2
CO_2	42.4
Other	0.84
TOTAL	100.00%

(5) The raw limestone feed to the process contains 5% free moisture.

(6) The weight ratio of limestone/anorthosite (dry basis) in the feed is 2/1.

(7) 15% of ground slurry will be +200 mesh and will be recycled as 50% solids from wet classification to wet grinding.

(8) The -200 mesh solids underflow from the thickener will contain 50% solids.

(9) The -200 mesh solids filter cake will contain 17% moisture.

(10) The 17% moisture filter cake of limestone and anorthosite will be reduced to 12% in a waste heat dryer. The heat will be supplied by the hot sinter kiln gases.

(11) The sinter kiln will be a rotary kiln.

(12) There is a 1% dust loss (calcined basis) from the sinter kiln. No Na_2O is vaporized and lost from the kiln.

(13) Coal with a heating value of 13,000 Btu/lb is used as the sinter kiln fuel. It is burned using 1% excess oxygen.

(14) 5% of the sinter out of the kiln will not "dust" and will be recycled as +20 mesh material to the sinter kiln.

(15) 75% extraction efficiency of Al_2O_3 is achieved in the leaching step.

(16) 24% extraction of Na_2O and 0% K_2O from the limestone/anorthosite mix is achieved.

(17) No CaO, Fe_2O_3, other, or MgO are extracted in the leaching step.

(18) Vacuum filtration is used to separate the pregnant liquor from the leach residue and 1.5 displacements of wash water are used to yield a 95% washing efficiency.

(19) Sufficient SiO_2 to yield 1 gram per liter SiO_2 in the pregnant liquor is extracted in the leaching step.

(20) The leach residue will contain 48% solids.

(21) 2% soluble Al_2O_3 is lost in the leach residue.

(22) DSP seeded desilication will be used.

(23) DSP will be $3Na_2O \cdot 3Al_2O_3 \cdot 5SiO_2 \cdot 5H_2O$.

(24) SiO_2 from desilication will be 0.035 gram per liter.

(25) DSP filter cake will contain 50% solids.

(26) Recycle DSP filter cake to desilication will not be washed.

(27) 100 gram per liter DSP seed will be recycled to desilication.

(28) DSP bleed filter cake to the sinter kiln will be completely washed.

(29) 80% CO_2 absorption efficiency will be achieved in carbonation.

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(30) Scrubbed carbonation gases will be saturated with water at 130°F.

(31) Alumina hydrate slurry will settle to 60% solids.

(32) Alumina hydrate filter cake will contain 75% solids.

(33) There is a 1% dust loss (calcined basis) from the alumina hydrate calcination kiln. A rotary kiln is used for this calcination.

(34) Sinter kiln gas scrubbers will remove 100% of contained solids.

(35) The scrubber water bleed will be at 2% solids.

(36) A multiple-effect evaporator (3-effect) is used to concentrate the spent liquor solution.

TABLE 4-5-1

ANORTHOSITE/LIME SINTER PROCESS FOR ALUMINA DAILY THERMAL REQUIREMENTS FOR 1,000 TON/D Al_2O_3

	100 LB/IN^2 (GA) STEAM, M LBS (881 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
SINTER PREPARATION			
DRYING	–	3,636	–
SINTERING	–	57,960	–
LEACHING			
LEACHING TANKS	2,904	–	–
DESILICATION			
DESILICATION TANKS	3,236	–	–
CALCINATION			
KILNS	–	3,907	–
EVAPORATION			
SPENT LIQUOR EVAPORATION (3-EFFECT)	4,373	–	4,093
SINTER KILN FLUE GAS PROCESSING			
WASTE HEAT FOR DRYER	–	-3,636	–
WASTE HEAT BOILER	-10,513	–	–
TOTALS	0	**61,867**	**4,093**

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 61,900 MM BTU/D *OR* 61.9 MM BTU/TON Al_2O_3

Table 4-5-2 (Sheet 1 of 5)

Alumina from Anorthosite/Lime Sinter Process Material Balance

1,000 TON/D Al_2O_3

Process Stream	1	2	3	4	5	6	7	8	9	10	11
Component											
Al_2O_3	1318	81	1423	14	1409	1591		375	1216	2161	2161
$Al_2O_3 \cdot 3H_2O$											
Na_2O	202	5	221	2	219	2360		199	2161	2857	2857
K_2O	50	12	62	1	61	61		61			
SiO_2	2687	141	2851	28	2823	2824		2800	24	851	851
CaO	583	5448	6031	60	5971	5971		5971			
MgO	15	21	36		36	36		36			
Fe_2O_3	102	19	121	1	120	120		120			
CO_2		4278	4278	10328		1317		747	570	619	619
Other	112	85	197	2	195	195		195			
H_2O	104	532	2142	3346		17719	16942	11217	23444	25789	25789
O_2				386							
N_2				18424							
Total	5173	10622	17362	32592	10834	32194	16942	21721	27415	32277	32277

All units are in short tons per day.

Table 4-5-2 (Sheet 2 of 5)

Alumina from Anorthosite/Lime Sinter Process Material Balance

Process Stream	12	13	14	15	16	17	18	19	20	21	22
Component											
Al_2O_3		1192	969	945	24	186	5		1000	181	4
$Al_2O_3 \cdot 3H_2O$						1930	1545	1545		385	385
Na_2O		2147	710	696	14	2196	65	6	6	2131	49
K_2O											
SiO_2		0.8	850	827	23	0.8	0.3	0.3	0.3	0.5	
CaO											
MgO											
Fe_2O_3											
CO_2		570	49	49		1350	39	3	3	1311	30
Other											
H_2O	136	23505	2420	2345	75	23570	890	521		22680	525
O_2											
N_2											
Total*	136	27415	4998	4862	136	29233	2547	2075	1009	26689	993

*Rounded to nearest whole number.

Table 4-5-2 (Sheet 3 of 5)

Alumina from Anorthosite/Lime Sinter Process Material Balance

Process Stream	23	24	25	26	27	28	29	30	31	32	33
Component											
Al_2O_3	177	5	182	182		182	1	13		1	13
$Al_2O_3 \cdot 3H_2O$											
Na_2O	2082	59	2141	2141	0	2141		2			2
K_2O								1			1
SiO_2	0.5		0.5	0.5		0.5	3	25		3	25
CaO							6	54		6	54
MgO											
Fe_2O_3								1			1
CO_2	1281	36	1317	1317	0	1317	938	9390	938		
Other								2			2
H_2O	22155	2028	24183	17719		17719	304	3042	265	490	4802
O_2							35	351	35		
N_2							1673	16751	1673		
Total*	25696	2128	27824	21360	0	21360	2960	29632	2911	500	4900

*Rounded to nearest whole number.

Table 4-5-2 (Sheet 4 of 5)

Alumina from Anorthosite/Lime Sinter Process Material Balance

Process Stream	34	35	36	37	38	39	40	41	42	43	44
Component											
Al_2O_3				1399		1646	1399	1399			
$Al_2O_3 \cdot 3H_2O$											
Na_2O				207		244	207	207			
K_2O				62		73	62	62			
SiO_2				2828		3327	2828	2828			
CaO				6031		7095	6031	6031			
MgO				36		42	36	36			
Fe_2O_3				121		142	121	121			
CO_2	9390			4278		5033	4278	4278			
Other				197		232	197	197			
H_2O	2649	451	4409	636	2469	5780	50847	15159	12054	35688	47742
O_2	351										
N_2	16751										
Total	29141	451	4409	15795	2469	23614	66006	30318	12054	35688	47742

Table 4-5-2 (Sheet 5 of 5)

Alumina from Anorthosite/Lime Sinter Process Material Balance

Process Stream	45	46	47	48	49	50	51	52	53	54	55
Component											
Al_2O_3	1399		1399	1483	1483	74		10		247	
$Al_2O_3 \cdot 3H_2O$											
Na_2O	207		207	231	231	12				37	
K_2O	62		62	64	64	3				11	
SiO_2	2828		2828	2972	2972	149				499	
CaO	6031		6031	6285	6285	314				1064	
MgO	36		36	38	38	2				6	
Fe_2O_3	121		121	126	126	6				21	
CO_2	4278		4278							755	188
Other	197		197	205	205	10				35	
H_2O	3105	1038	2067				1659	1056	6464	2675	190
O_2											35
N_2											1673
Total	18264	1038	17226	11404	11404	570	1659	1066	6464	5350	2086

4.5.8 Equipment List

ALUMINA FROM ANORTHOSITE VIA LIME-SINTER PROCESS

Ore and Limestone Preparation Area

Truck dump hopper
Truck dump apron feeder
Vibrating grizzly apron feeder
Vibrating grizzly
Jaw crusher, ore
Ore pile conveyor and stacker - reclaimer
Water spray system
Raw ore pile feeder
5 inch ore conveyor
Vibrating screen
Vibrating screen conveyor
Hydrocone crusher conveyor
Fine ore bins
Fine ore to bin conveyor
Chutes and hoppers
Limestone truck dump hopper
Limestone truck dump apron feeder
Limestone vibrating grizzly apron feeder
Limestone vibrating grizzly
Limestone jaw crusher, limestone
Limestone pile conveyor and stacker-reclaimer
Water spray system
Limestone conveyor
Limestone vibrating screen
Limestone vibrating screen conveyor
Limestone hydrocone crusher
Limestone hydrocone crusher conveyor
Fine limestone bins
Fine limestone to bin conveyor
Fine ore weighfeeders
Limestone weighfeeders
Fine ore rod mill feed conveyors
Limestone rod mill feed conveyors
Rod mills
Classifiers
Ball mills
Classifier pumps
Dust collection system
Hydrocone crusher
Limestone pile feeder

EQUIPMENT LIST (Cont)

Ore Thickening, Filtration, Drying, and Pelletizing Area

Ore thickeners
Ore thickener rakes
Ore thickener underflow pumps
Ore thickener overflow pumps
Ore rotary vacuum filters
Filter cake to dryer conveyor
Filtrate receiver
Filtrate pumps
Vacuum pumps
Partial dryer discharge apron feeder
Filter cake rotary dryer
Cyclone dust collector
Baghouse dust collector
Partially dried cake bucket elevator
Partially dried cake screw conveyor
Rotary disc pelletizers
Pellet conveyors
Pellet bucket elevator
Pellet surge bin
Chutes and hoppers

Sintering, Soaking and Screening Area

Sinter kiln apron feeders
Sintering kilns
Sintering kiln coolers
Sintered ore apron feeder
Soaking kilns
Soaking kiln coolers
Soaked ore discharge screw conveyor
Soaked ore bucket elevators
Soaked ore rejects conveyor
Soaking kiln dust collection
Screened ore bucket elevator
Dusted sinter surge bin
Dusted sinter weighfeeder
Leach feed conveyor
Soaking kiln apron feeder
Chutes and hoppers
Soaked ore screens, chutes

EQUIPMENT LIST (Cont)

Leaching, Leach Filtration, Desilication, Vacuum, and Filtration Area

Leach tanks
Leach tank covers
Leach tank agitators
Leach tank steam coils
Leach tank pumps
Leach surge tank
Leach surge tank agitators
Leach product pumps
Leach vacuum disc filters
Leach residue conveyors
Filtrate receiver
Vacuum pump
Pregnant liquor pumps
Desilicator tanks
Desilicator agitators
Desilicator steam coils
Desilicator transfer pumps
1st stage rotary vacuum filter
1st stage desilicator produce (DSP) conveyor
2nd stage rotary vacuum filter
2nd stage DSP conveyor
Filtrate receiver
Vacuum pump
DSP filtrate pumps
DSP filtrate surge tank
DSP filtrate surge pumps
Pressure filters and chutes
Collecting sluice
Vibrating screen and bin
Press cake tank
Repulped slurry pumps

Carbonation (Flocculation Preparation and Wasteheat Boilers) Area

Flocculant system
Feed hoppers
Screw feeders
Flocculant mix tank
Flocculant mix transfer pump

EQUIPMENT LIST (Cont)

Flocculant storage tank
Flocculation solution pumps
Carbonator vessels
Carbonator underflow pumps
Waste heat boilers
Boiler feed water pumps
Spray cooler scrubber and pumps
Spray scrubber stack
Scrubber compressor intercoolers
Soda ash storage tank
Soda ash pneumatic conveyor system
Soda ash weighfeeder
Soda ash mix tank
Soda ash conveyor
Soda ash mix tank agitator
Soda ash mix tank steam coils
Soda ash mix tank pumps

Spent Liquor Evaporation, Product Thickening, Calcining, and Storage Area

Evaporation test tank
Evaporator feed pumps
Evaporation system
Digestion test tank
Spent liquor tansfer pumps
Evaporation product pumps
Evaporation hotwell
Evaporation hotwell pumps
Evaporation condensate pumps
Primary thickeners
Primary thickener underflow pumps
Primary thickener wash tanks
Primary thickener wash tank stationary screen
Primary thickener wash tank slurry pumps
Secondary thickeners
Secondary thickener underflow pumps
Secondary thickener surge tank
Secondary thickener surge underflow pumps
Tertiary thickener
Tertiary thickener rakes

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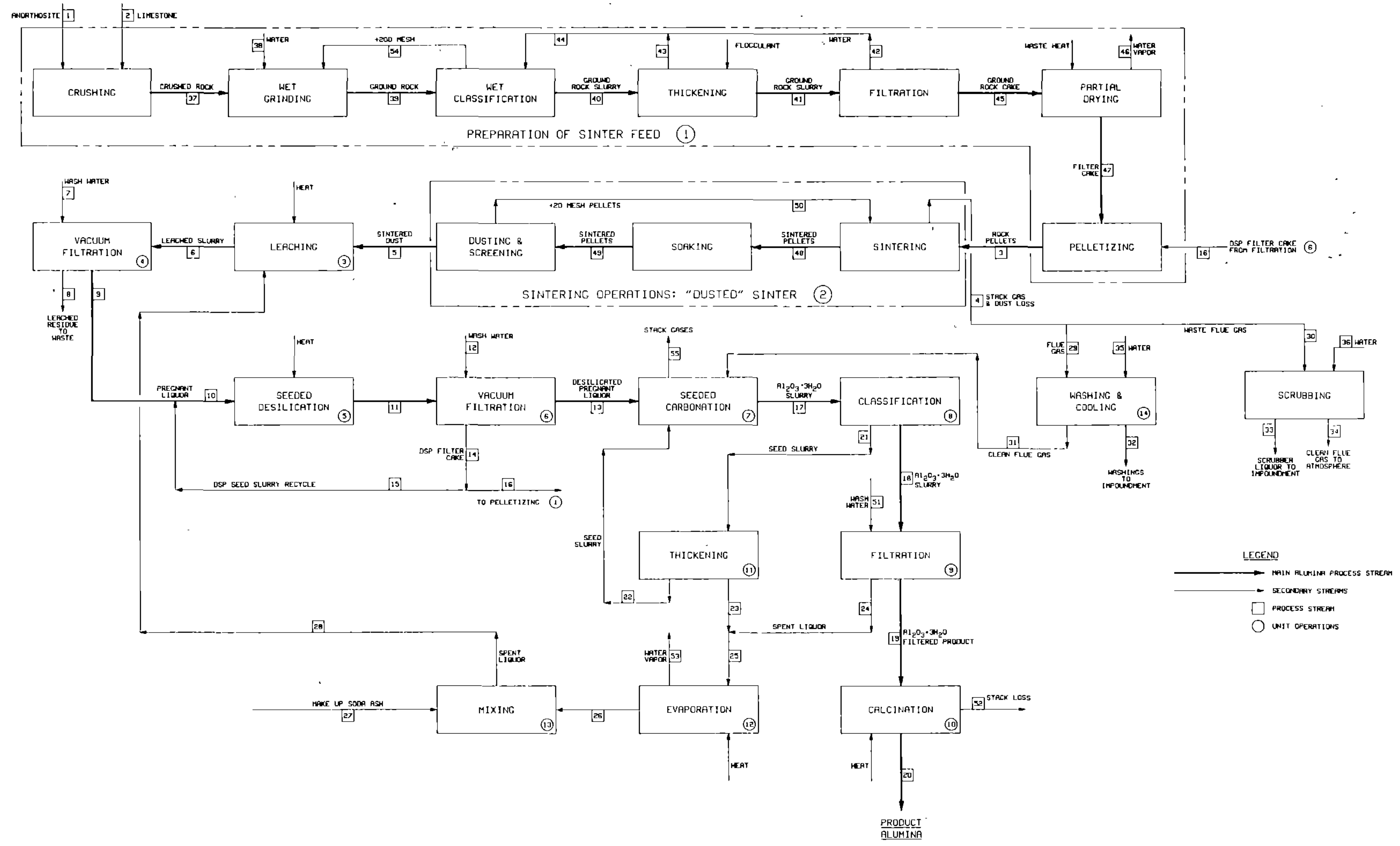
EQUIPMENT LIST (Cont)

Tertiary thickener underflow pumps
Tertiary thickener overflow pumps
Tertiary thickener seed storage tanks
Tertiary thickener seed transfer pumps
Wash liquor tanks
Wash liquor pumps
Hydrate tank
Hydrate pumps
Slurry density tank
Slurry density pumps
Hydrate filters
Filtrate receiver
Filtrate pumps
Wash water receiver
Wash water pumps
Vacuum pumps
Hydrate tank overflow pumps
Calciner feed conveyor
Rotary calciners
Rotary coolers
Fluo-solids cooler
Product conveyor
Cyclone dust collector
Electrostatic precipitator
Alumina silos
Chutes and hoppers

Utilities Area

Cooling tower and auxiliaries



FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-5-2

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-5-1

NO	DATE	REVISION	BY CHK	APP	APP.

NOTES

DESCRIPTION COST ACCOUNT

WORK COVERED BY THIS DRAWING CHARGED TO COST ACCOUNT ABOVE

CONSTRUCTION APPROVAL

APPROVAL DATE

SCALE. DATE

DESIGNED BY

DRAWN BY ADS

CHECKED BY

APPROVED BY

APPROVED BY

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO J0265048

ALUMINA FROM ANORTHOSITE

LIME SINTER PROCESS

JOB No. 76161-001

FIGURE NO. 4-5-2

REVISION R-0

NOT REPRODUCIBLE

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4.6 TECHNICAL APPRAISAL: ALUMINA FROM ALUNITE VIA REDUCTION ROASTING - MODIFIED BAYER PROCESSING

4.6.1 Summary and Conclusions

The process being evaluated for the extraction of reduction-grade alumina from alunite is illustrated in summary form on the following page. It includes the following steps:

(1) Crushing and grinding of the raw ore to produce a particle size distribution suitable for processing in fluidized solids equipment.

(2) Roasting the ore at approximately 1,100°F, employing fluidized solids techniques, and using powdered coal under oxidizing conditions as fuel for the removal of free and combined water.

(3) Roasting the product of the first roast further under reducing conditions in the presence of coal gas as a reductant to reduce a major fraction of the sulfate associated with aluminum to SO_2 gas.

(4) Roasting the solid product from step 3 for an additional short period of time under oxidizing conditions using coal gas as a fuel to convert any sulfides that may have been formed in step 3 back to oxides.

(5) Leaching the potassium sulfate content of the alunite together with any unreduced sulfate associated with the alumina from the solid product of step 4 with KOH.

(6) Separating and washing as completely as practical the residual solids to remove the potassium and sulfate.

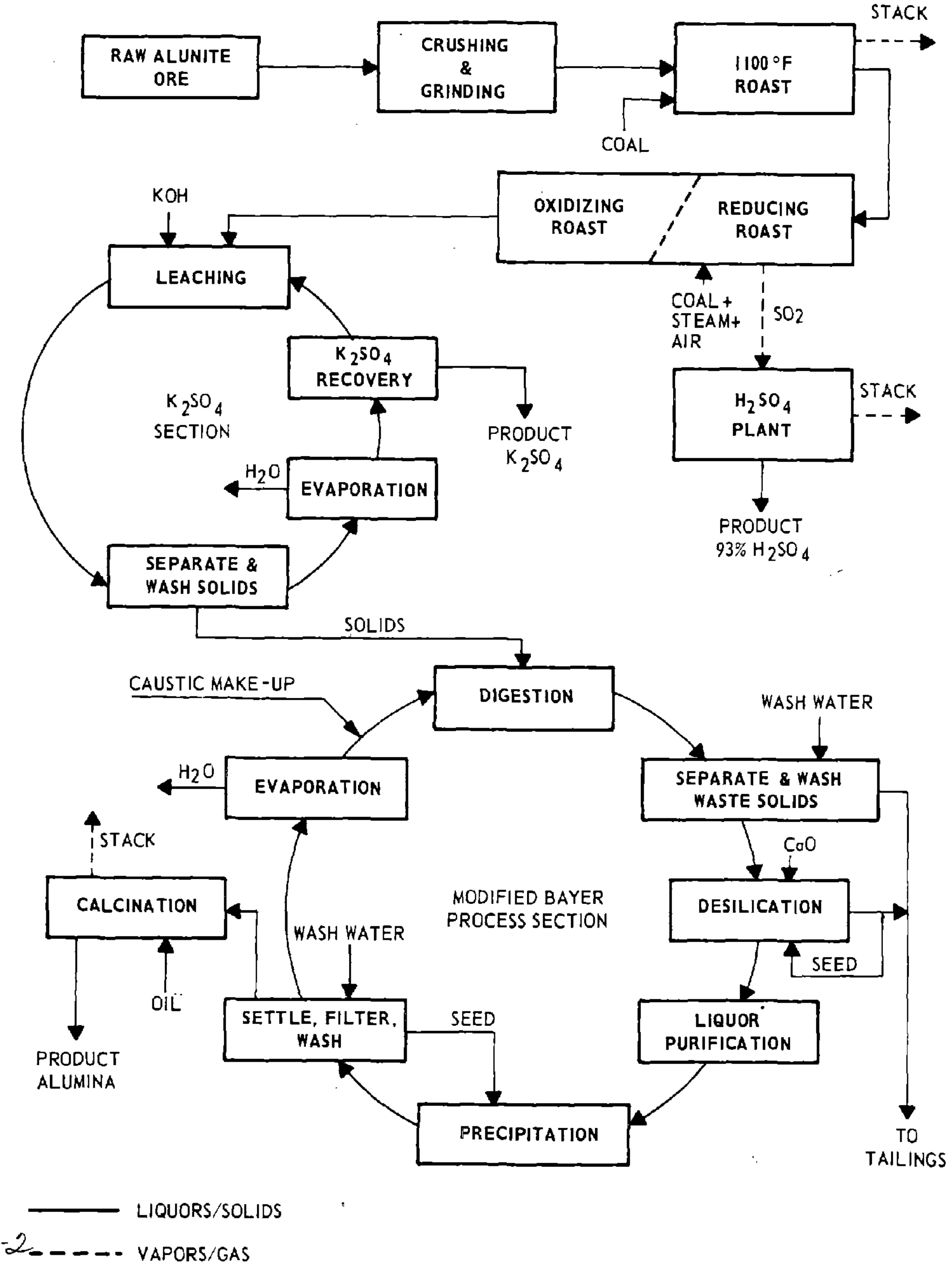
(7) Leaching with caustic soda by means of suitably modified Bayer process technology, the alumina from the washed solids of step 6.

(8) Once again, separating and washing the residual solids, and sending the washed solids to tailings disposal.

(9) Treating the leach liquor from step 7 to remove dissolved silica in the form of precipitated sodium aluminum calcium silicate; settling the solids and filtering them with some of them being recirculated as seed crystals; and sending the net production to waste disposal.

FIGURE 4-6-1

ALUMINA, K_2SO_4 AND H_2SO_4 FROM ALUNITE VIA REDUCTION ROASTING, MODIFIED BAYER EXTRACTION



4-6-2

(10) Precipitating alumina trihydrate from the purified solution.

(11) Filtering and washing the alumina trihydrate.

(12) Calcining the alumina trihydrate to product alumina.

(13) Concentrating the potassium sulfate leach liquor and washings from steps 5 and 6 by evaporation and cooling them to crystallize potassium sulfate.

(14) Recovering the crystalline potassium sulfate by centrifuging, drying, compacting, and sizing to obtain product sulfate of potash; bleeding off a portion of the mother liquor for the control of impurities; and then returning the major fraction of it to potassium sulfate leaching.

(15) Converting sulfur dioxide bearing gases from step 3 in a conventional sulfuric acid plant to product 93% H_2SO_4.

Information about the process upon which the evaluation is based has been obtained primarily from the Bureau of Mines in the form of a Draft Environmental Statement prepared by the Bureau of Land Management describing proposed actions by Alumet. A limited amount of supplementary and confirming information has been obtained from other publicly available literature.

More steps are required in the manufacture of alumina from alunite than from some other alumina-bearing raw materials, because alunite contains (in addition to alumina) potassium, sulfate, and silica as major constituents. Capital and energy must inevitably be provided in any alumina process starting with alunite for process unit operations separating the potassium and the sulfate from the substantial amount of silica gangue, and from the alumina, and then for converting these by-products into some marketable form. It is important to note that the market values of sulfuric acid and potassium sulfate, the easiest forms in which to dispose of the sulfur and potassium, are low in relation to alumina.

For every ton of alumina produced from alunite, 1 ton of sulfuric acid and 0.73 ton of potassium sulfate will also be produced. The marketability of large tonnages of these materials raises questions as to what limitations these materials might place on the amount of alumina which could be produced commercially from alunite.

The total process energy consumption is approximately 26.1 x 10^6 Btu/ton alumina. It is advantageous that approximately 22.2 x 10^6 Btu of this, including both directly applied process energy and the requirement for steam generation may be supplied by the combustion of coal. The remaining 3.9 x 10^6 Btu are required for the direct-fired calcination of alumina trihydrate and must be supplied by the combustion of oil or other clean fuel.

Insofar as is known at the present time quantitative reduction of the sulfate associated with aluminum in the entering ore is impractical. Potassium hydroxide equivalent to this unreduced sulfate is therefore supplied in the leaching step following the reducing roast in order to solubilize the unreduced sulfate. This imposes a substantial economic penalty on the process, because the value of the potassium sulfate obtained from conversion of the potassium hydroxide is much less than the cost of this reagent.

Most of the silica gangue in the entering ore is present in a non-reactive form of relatively coarse particle size. However, opal and kaolin have been reported to occur in association with the Utah alunite deposit, and the nature of the geochemical process by which alunite is formed is such that these minerals are likely to be in close association in any alunite deposit. Both the opal and kaolin after calcination will be reactive towards the caustic Bayer liquor. Kaolin which dissolves will contribute some alumina towards the desilication product (DSP) losses. The solution of silica from the opal fraction will cause losses of both soda and alumina in the formation of DSP. These losses in the form of desilication product are expected to be substantial in the process being evaluated here.

Solids entering the Bayer process section are expected to contain only 15-20% extractable alumina. The relatively large amount of solids which must be handled, processed, washed, and discarded in order to obtain a unit of alumina is expected to contribute to high costs for the overall process.

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It is expected that residual sulfate in the solids entering the Bayer section of the process will tend to build up in the recirculating Bayer process liquor. Some means for removal of this sulfate from the Bayer liquor will probably have to be devised.

The Bayer alumina extraction section of the overall process will require further study in order to meet reduction-grade alumina specifications while achieving an adequately high alumina extraction together with acceptably low soda and alumina losses in desilication. The control of other impurities which are expected to be more troublesome than in the Bayer extraction of alumina from bauxite will also require study. Another question requiring special mention is whether the presence of a small amount of potassium oxide in alumina produced from alunite will cause difficulties in reduction cell operation. A recent published report indicates that acceptable reduction cell operation can be achieved with this alumina, but further study is required.

It is considered probable, after the above-mentioned studies, that alumina meeting reduction-grade chemical purity and physical property specifications can be produced from alunite.

It is believed that the production of alumina from alunite can be engineered to meet applicable environmental regulations. The presence of sulfate in the alunite will contribute substantially to the cost of the provisions for environmental control.

The overall recovery of alumina from alunite by the process being evaluated is 80-85%. If alunite is to be a source of alumina, it appears desirable to design a process that would be capable of achieving a higher recovery of alumina from the ore, that would not require KOH, that would produce elemental sulfur rather than sulfuric acid, and that would more effectively deal with reactive silica. It is possible that an acidic process might be developed to achieve these goals, although no such process is known at present. Even if such a process were developed, it would be handicapped by capital and energy requirements for separation and recovery of the relatively low value potassium and sulfur, as well as by the low grade of the best alunite ore with respect to the valuable alumina.

Any process technology developed for the production of alumina from alunite, despite the proving of substantial reserves of alunite ore in Utah, can be of only limited applicability in a worldwide sense, because proven reserves of high-grade alunite are very limited.

4.6.2 Background

Interest in alunite as a raw material for the production of alumina has existed for many years and received renewed impetus during national emergencies that saw restrictions in the bauxite supply. Early investigators noted that the alunite component of an ore could be rendered quite chemically reactive by a relatively simple calcination at a moderate temperature. The potassium and sulfate contents of the alunite, which upon intensive study of alumina production alternatives prove to be a liability, at first appeared attractive and easily recoverable by simple known technology.

The development of alunite as a raw material for alumina was always handicapped until recently by the widely held opinion that reserves of high-grade alunite were small. The discovery about 1971 of much larger reserves in Utah containing 30% or more alunite led to renewed efforts to develop an economical process for extracting the alumina and other values. These efforts are described in a conceptual process being evaluated here.

4.6.3 The Process

4.6.3.1 Summary

Entering alunite ore is crushed and ground to prepare it for roasting employing fluidized solids techniques. The prepared alunite is first roasted under oxidizing conditions at about 1,100°F using powdered coal as a fuel to remove free and combined water. It is next roasted to reduce a major fraction of the sulfate associated with alumina to SO_2 gas, but also with the goal of minimizing conversion of the active alumina so produced into a subsequently insoluble form. Next the ore is again roasted briefly under oxidizing conditions using powdered coal as fuel to reconvert any sulfides formed back to oxides. The roasted ore is now leached with recycled potassium sulfate solution to which has been added KOH equivalent to any unreduced sulfate associated with alumina. The purpose of this step is to dissolve the naturally present K_2SO_4 together with all remaining sulfate. The residue, after washing out the soluble sulfates, becomes modified Bayer process feed.

The Bayer process, using a caustic leach, must be designed to extract the reactive alumina while minimizing extraction of silica from the large mass of waste solids associated with the alumina. Provision must be made for removal of silica which does dissolve and for the control of sulfate and other impurities.

The soluble sulfate bearing first leach liquor and washings are processed for K_2SO_4 recovery. SO_2-bearing gases are converted to H_2SO_4 in a conventional acid plant.

4.6.3.2 Crushing, Conveying, and Storage of Raw Ore

Alunite has the chemical formula $KAl_3(OH)_6(SO_4)_2$, a density of 2.6-2.8, and a Mohs' hardness of 3.5-4. It is formed by the action of natural sulfuric acid solutions acting on rocks rich in potash feldspar, and occurs in massive form in admixture with the silica coproduct from decomposition of the feldspar. Varying amount of feldspar, kaolin, and other minerals may also be present. The first step in the processing of alunite ore therefore is to crush it from the as-quarried form to a size suitable for storage, conveying, and further size reduction in preparation for roasting. This process area, in view of the physical properties of the raw ore, is not expected to offer unexpected technical difficulties and may be engineered based upon known technology.

4.6.3.3 Fine Crushing and Dry Grinding

It is expected that the most cost-effective technology for accomplishing the roasting of the ore will be the employment of fluidized solids techniques. The fine crushing and dry grinding operation accepts the coarsely crushed raw ore and reduces it to a controlled particle size distribution suitable for use in fluidized solids calciners. Here, again, no technical difficulties are expected. It is believed the fine crushing and grinding operation can be designed and operated on the basis of known technology.

4.6.3.4 First Roast for Removal of Free and Combined Water

The properly sized feed passes to the first fluidized bed roaster which is maintained at about 1,100°F by the combustion of directly injected powdered coal and air. The overall chemical reaction for the removal of combined water may be represented by the equation

$$KAl_3(OH)_6(SO_4)_2 \longrightarrow Al_2O_3 \cdot KAl(SO_4)_2 + 3H_2O \uparrow$$

even though discrete units of Al_2O_3 probably do not actually exist in the calcine.

A residence time of two hours is postulated to insure complete removal of combined water from calcine leaving the roaster. It is possible that in commercial practice this roasting could be carried out in stages in order to obtain complete removal of the combined water (avoid short-circuiting of unreacted solids) with a much shorter total residence time.

Particles of coal during combustion must attain temperatures far higher than 1100°F, but this apparently has no adverse effect upon the ore being calcined. Ash remaining in the calcine will be substantially inert in following process operations. Provided a temperature sufficient to achieve a reasonable calcination rate has been reached, insofar as can be determined from the literature, the calcination is not extremely sensitive to either temperature or residence time. It is however important to operate the calcination always under oxidizing conditions and below about 1300°F in order to minimize, in this step, decomposition of the sulfate in the ore. Fluidized solids techniques are known to be well suited for meeting the conditions described above that are required for this calcination. It is expected that this calcination may be effectively accomplished using known technology and without encountering severe technical difficulties.

4.6.3.5 Reducing Roast for Removal of Sulfate Associated with Alumina

Calcine from the preceding roast passes hot to a fluidized reducing roast operating, according to the Russian literature, adiabatically at about 1000°F with a one-hour residence time and using a mixture of CO and H_2 as the reducing agent. The overall desired chemical reactions are:

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$$2\left[Al_2O_3.KAl\,(SO_4)_2\right] + 3CO \rightarrow 3Al_2O_3.K_2SO_4 + 3SO_2 + 3CO_2$$

or

$$2\left[Al_2O_3.KAl\,(SO_4)_2\right] + 3H_2 \rightarrow 3Al_2O_3{\cdot}K_2SO_4 + 3SO_2 + 3H_2O$$

The degree of sulfur removal tends to increase with increasing roast temperature, but unfortunately the alumina also tends with increasing roast temperature to be converted to a caustic-insoluble form by a mechanism not fully understood. Again, fluidized solids techniques appear to offer the best means of closely controlling the roasting conditions so as to achieve the best possible sulfur removal while minimizing deactivation of the alumina. The Russian literature reports approximately 80% sulfur removal with approximately 80% of the alumina remaining in the soluble form to be the best obtainable result.

Potassium hydroxide or ammonia equivalent to the unreduced sulfate associated with alumina must be supplied in a subsequent process operation, and the loss of as much as 20% of the alumina in the ore by conversion to a caustic-insoluble form is undesirable. The reduction roasting technique has been studied intensively in Russia. So far as is known, the technical difficulties described above associated with reduction roasting remain and based on the amount of work reported on this subject the prognosis for future solution is considered poor.

4.6.3.6 Reoxidizing Roast

The reducing roast tends to convert some oxides present in the ore--and particularly iron--to sulfides. These sulfides represent a loss of sulfur, and they would interfere with the operation of the Bayer process recovery of alumina. Solids discharged from the reducing roast are therefore delivered hot to a final fluidized roast under oxidizing conditions where the following reaction takes place:

$$2FeS + 3\tfrac{1}{2}O_2 \longrightarrow Fe_2O_3 + 2SO_2$$

This roasting step is reported to be directly fired with a small amount of powdered coal. The temperature is estimated to be 1100°F, and the residence time is estimated at 30 minutes. No severe technical difficulties are anticipated in connection

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with operation of this step, and design of the equipment required for it should be possible based upon known technology.

4.6.3.7 Dissolve Potassium Sulfate

The reoxidized calcine is mixed with recycled K_2SO_4 solution wherein the K_2SO_4 component of the calcine dissolves:

$$3Al_2O_3 \cdot K_2SO_4 + \text{Solution} \rightarrow 3Al_2O_3 + K_2SO_{4\,\text{soln.}}$$

Potassium hydroxide is added to the recycle solution to dissolve unreduced sulfate associated with alumina, simultaneously freeing for solution existing K_2SO_4 present in the alunite calcine structure:

$$Al_2O_3 \cdot KAl(SO_4)_2 + 3KOH_{\text{aq.}} \rightarrow Al_2O_3 \cdot Al(OH)_3 + 2K_2SO_{4\,\text{aq.}}$$

This procedure is effective for the removal of potassium and sulfate from the roasted solids. Its primary disadvantage is that the cost of the KOH used to combine with the remaining sulfate associated with alumina is much greater than the value of the resulting K_2SO_4.

The leaching procedure is simple and no major technological difficulties are anticipated in the operation of this step. It is expected that the required equipment can be designed and constructed on the basis of known technology.

4.6.3.8 Separate, Wash, and Remove Undissolved Solids

Solids remaining after leaching of the potassium and sulfate are granular in nature. They may be filtered and washed on belt extractors. No technical difficulties are expected in this operation and no new technology is required.

4.6.3.9 Modified Bayer Process Dissolution of Alumina

The solids remaining after leaching and washing out sulfate and potassium consist of approximately 20% alumina with the balance comprising primarily silica, together with small amounts of Fe_2O_3 and TiO_2. Some K_2SO_4 will also be present. These solids pass to a modified Bayer process using caustic soda to extract the alumina. It is necessary to design the Bayer extraction very carefully to maximize the extraction of alumina while minimizing solution of the relatively large mass of silica present, some of which is reactive. This is a technical problem requiring further study prior to the design of a demonstration plant for the production of alumina from alunite via this process.

4.6.3.10 Separate, Wash, and Remove Insolubles

The slurry from digestion is thickened in conventional thickeners. The thickener underflow is then washed in a multistage CCD system to recover the soda values before the mud is pumped to waste. No critical technical difficulties are expected in this operation, and the required equipment may be designed on the basis of known technology.

4.6.3.11 Liquor Purification

An amount of silica larger than would be acceptable in the product alumina, or than could be controlled by means of an economically acceptable bleed stream, is certain to be dissolved along with the alumina. Sulfate and potassium are also expected to build up in the recycling Bayer liquor unless means are provided for their control. Carbonates and may also be present.

Control of dissolved silica will be provided by a desilication step in which the pregnant liquor is held at elevated temperature with gentle agitation for a period of hours in the presence of desilication product seed crystals. In a conventional Bayer process operation in the absence of lime, the seed crystals would grow, removing silica from the solution as a solid of the approximate expected composition:

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \sim 2H_2O \cdot 1/3Na_2O \; (\sim \tfrac{1}{2}CO_2, \sim \tfrac{1}{2}Al_2O_3)$$

Thus, each unit of SiO_2 which must be removed from the solution would carry out of solution 1.0 units Al_2O_3 and 1.18 units soda. In the presence of lime it is expected that the normal desilication product will react partially to liberate soda and form hydrogrossularite, which has the approximate formula

$$3CaO \cdot Al_2O_3 \cdot YSiO_2 \cdot (6-2Y)\, H_2O$$

where Y may have a value ranging from slightly more than one to considerably less than one. The amount of lime stated in the Draft Environmental Statement may not be adequate for recovery of all of the soda in the desilication product, or some of this material may be nonreactive to lime. However, any significant loss of alumina and of soda in desilication product could impose a substantial economic penalty on the process. These potential losses emphasize the need for further study of the digestion operation with the goal of maximizing alumina extraction while minimizing the extraction of silica. Determination of the optimum relationship between the amount of desilication product seed recycled, lime addition, holding time, temperature, and intensity of agitation required to secure adequate desilication will also require further study.

The slurry at the conclusion of desilication will be classified and thickened. An appropriate amount of seed will be returned to desilication. The net production of desilication product crystals will be sent to waste. A polish filtration must be provided for the pregnant liquor proceeding to precipitation. The separation, partial recycling, and partial discard of the desilication product are not expected to present severe technical problems and may be engineered on the basis of known technology.

The removal of sulfate from the recycling Bayer liquor will be required but has not been studied. Precipitation as $BaSO_4$ would be expected to provide acceptable control but would require provision for recovery and regeneration of the costly barium reagent.

Carbonate control may be achieved by causticization with lime or may be achieved with barium, again with the requirement of regeneration if barium is used. Carbonate control has not been studied, and no provision has been made for it in the flowsheet (Figure 4-6-1). Similarly, there has been no study or provision made for the control of any organic carbon.

The extent to which potassium may build up in the recycling Bayer liquor, its effect on the operation of the Bayer extraction, and the amount of it which will appear in the product alumina for a given potassium level in the Bayer liquor have not been studied. Also unknown is the level of K_2O which may be tolerated in reduction cell feed. Further study is required.

4.6.3.12 Alumina Trihydrate Precipitation

The precipitation of alumina trihydrate is expected to be accomplished much in the manner of conventional Bayer process technology using seeded crystallization. Solid alumina trihydrate in the slurry leaving precipitation is classified in a settling operation. Slurry containing the coarser trihydrate particles is thickened and the underflow filtered. The solids are washed and sent to calcination. Slurry containing the smaller particle sizes is thickened with the underflow containing the seed returning to precipitation.

The precipitation and solid-liquid separation operations will be very similar to those carried out in a Bayer plant operating on bauxite provided that control has been achieved over the various impurities discussed above which may be present in the liquor to reduce their concentrations to the levels present during precipitation in a conventional Bayer plant. Hopefully, extraction of alumina can also be managed to present to precipitation a pregnant liquor of proper alumina and caustic concentration at the temperature required to produce a product of requisite granulometry. Since this hope may not be entirely realized and economic considerations or technical necessity will dictate attempting to operate with liquor impurity levels different from those encountered in a Bayer plant operating on bauxite, the precipitation step will require further study using actual liquors derived from alunite processing on a cyclic basis before the design of a demonstration plant can be undertaken with confidence.

4.6.3.13 Alumina Trihydrate Calcination

Calcination of the washed alumina trihydrate can be accomplished using known technology in a manner similar to the calcination of trihydrate derived from bauxite. The use of fluidized solids techniques is the probable choice. A clean fuel such as oil is required for this direct-fired operation. No severe technical difficulties are expected.

4.6.3.14 Spent Liquor Evaporation and Recycle

Spent liquor from precipitation passes to multiple-effect evaporation where it is reconcentrated for water balance control of the Bayer process operation prior to recycle to alumina extraction. Makeup caustic is added to the liquor proceeding to extraction.

It is believed unlikely that major technical difficulties will be experienced in evaporation of the spent liquor, but operation with differing levels of impurities than are present in conventional Bayer liquors could cause scaling, corrosion, or other problems. Study of the evaporation of spent liquor produced in a smaller-scale cyclic operation is recommended prior to the design of a demonstration alumina plant based on alunite in order to verify predicted conditions of operation.

4.6.3.15 Sulfuric Acid Production

Sulfur dioxide gas produced during the reducing roast is cooled, washed, dried, oxidized to SO_3 and then absorbed in 93% H_2SO_4 to make 98% acid. This acid passes to the gas drying step to regenerate 93% H_2SO_4, which is also the product acid.

The acid plant is expected to be designed and built entirely on basis of known technology, and no severe technical difficulties are anticipated.

4.6.3.16 Potassium Sulfate Evaporation

The combined potassium sulfate-bearing leach liquor and washings are concentrated by multiple-effect evaporation for water balance control of the potash recovery section and to prepare pregnant liquor for potassium sulfate recovery. It is considered unlikely that severe technical difficulties will be experienced in the operation of this process section. Design of a demonstration scale facility is believed possible on the basis of known technology.

4.6.3.17 Potassium Sulfate Recovery

The solubility of K_2SO_4 decreases sharply with decreasing temperature. Hot concentrated pregnant K_2SO_4 solution from evaporation passes to a cooling crystallizer for the production of K_2SO_4 crystals. The crystals are recovered by centrifuging, dried, compacted, and sized to meet physical specifications set by the market place.

Some sodium is present as a substitute for potassium to a limited extent in the alunite molecule. This sodium appears in solution with the potassium, but is undesirable in the product K_2SO_4. Fortunately, the solubility of Na_2SO_4 changes very little with temperature, so that by proper control of operating conditions most of it can be held in solution during crystallization of the K_2SO_4. The concentration of Na_2SO_4 will therefore be enriched in the barren liquor remaining after recovery of K_2SO_4. A bleed stream is taken and sent to disposal at this point to control the buildup of Na_2SO_4. Unfortunately, the barren liquor still contains K_2SO_4, so the loss of a substantial amount of K_2SO_4 in the bleed stream must be accepted. The remaining major fraction of the barren liquor is recirculated to K_2SO_4 leaching.

No major technical difficulties are anticipated in the potassium sulfate recovery operation. It is expected that a demonstration plant-scale potassium sulfate recovery operation could be designed on the basis of known technology.

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4.6.4 Energy Requirements

The net energy requirement to process for the manufacture of alumina from alunite via reduction roasting and a modified Bayer extraction are as follows:

	Btu x 10^6 per ton Product Alumina
Dehydrating/Reduction Roast	15.2
Oxidizing Roast	0.5
Alumina Trihydrate Calcination	3.9
Steam	6.5
	26.1

Energy requirements for both roasts and steam generation may be met by the combustion of coal if desired. A clean fuel such as oil must be used for the alumina trihydrate calcination.

Energy consumption is approximately 26 x 10^6 Btu/ton alumina because in addition to recovery of alumina by a modified Bayer process, there are substantial requirements for head-end processing before the feed enters the Bayer process. Overall energy requirements are increased because of the low grade of the ore with respect to alumina and the mediocre recovery of alumina; i.e., a relatively large mass of ore must be processed to recover a unit of alumina.

4.6.5 Environmental Control

The Environmental Impact Statement discusses environmental control problems encountered in the processing of alunite in considerable detail. In essence, impoundment is planned for all aqueous wastes. Scrubbing is planned for gases containing oxides of sulfur or dust. The environmental control measures described in the report, although costly, appear to be adequate. The presence of sulfur in the ore contributes in an important way to the total cost of environmental control due to the requirement for control of SO_2 emissions and waste water soluble sulfates.

The waste solids sent to disposal will comprise silica, small amounts of unreacted accessory minerals, and iron oxide. The silica will not be excessively hydrated, and these waste solids should make a good subsoil provided small amounts of soluble sulfate which may be expected to leach from them can be adequately contained.

4.6.6 Alumina Product Quality

It is believed possible, by using a modified Bayer process to produce alumina meeting reduction quality chemical specifications with the possible exception of Fe_2O_3 and K_2O content. The product alumina will be similar in physical properties to other Bayer aluminas. Unanswered questions are the time required to secure adequate desilication, the soda and alumina losses which must be accepted in this step, and the relative difficulty that may be encountered in meeting particle size specifications.

4.6.7 Process Assumptions Used to Estimate the Heat and Material Balance

(1) The heat and material balance is based on 1,000 ton/d of alumina.

(2) Ore recovery (Al_2O_3 basis) through K_2SO_4 leach is 97%.

(3) Al_2O_3 is 90% soluble in NaOH leach.

(4) Al_2O_3 recovery in caustic refining section is 97%.

(5) Alunite ore contains 5.2% H_2O of which 5% is removed in drying.

(6) During ore drying 4.5% of $Al_2(SO_4)_3$ in the alunite decomposes.

(7) The reduction of the $Al_2(SO_4)_3$ is performed by coal gas.

(8) The coal gas used in 7 above is burned in excess air to provide the heat and O_2 for reoxidation of the sulfides formed in 7 above.

(9) The redox operation converts 92% of the residual $Al_2(SO_4)_3$ to Al_2O_3.

(10) Coal ash (13%) from ore drying and redox remains in the ore and is inert.

(11) A 2% KOH excess is used to convert residual $Al_2(SO_4)_3$ to Al_2O_3.

(12) SiO_2 contained in the ore dissolves to the extent of 0.5% in the caustic digest.

(13) All soda in the caustic refining section is assumed to be caustic soda.

(14) Dissolved SiO_2 is converted to 2 $NaOH \cdot Al_2O_3 \cdot SiO_2$ (DSP) for removal.

(15) DSP filter cake contains 33% H_2O.

(16) Residual ore (primarily SiO_2) is rejected at 40% solids.

(17) Solids feed to caustic digest contain 15% free H_2O.

(18) Alumina/caustic (A/C, caustic as Na_2CO_3) is 0.4 in caustic digest feed liquor and 0.65 in caustic digest exit liquor.

(19) Caustic concentration (as Na_2CO_3) is 220 g/l in digestion.

(20) The chemical analysis of the alunite feed is as follows:

Al_2O_3	9.86%
SiO_2	56.11
Fe_2O_3	3.50
$Al_2(SO_4)_3$	16.53
K_2SO_4	8.40
Na_2SO_4	0.38
H_2O	5.22
Total	100.00%

TABLE 4-6-1

ALUMINA FROM ALUNITE
DAILY THERMAL REQUIREMENTS
FOR 1,000 TON/D Al_2O_3

	100 LB/IN^2 (GA) STEAM, M LBS (881 BTU/LB)	FUEL, MM BTU	COOLING WATER, M GALS
ORE PREPARATION			
DEHYDRATING/REDUCTION ROAST	–	15,230	–
OXIDATION ROAST	–	530	3,667
SULFURIC ACID MANUFACTURE			
SO_2 COOLING	–	–	454
ACID COOLING	–	–	237
K_2SO_4 PREPARATION			
SOLUTION EVAPORATION	909	–	1,763
SOLIDS DRYING	588	–	–
Al_2O_3 PREPARATION			
DESILICATION	3,185	–	–
PRECIPITATION	–	–	2,250
CALCINATION	–	3,907	850
CAUSTIC EVAPORATION	2,318	–	4,047
OTHER	329	–	946
TOTALS	**7,329** **(6,457 MM BTU)**	**19,667**	**14,214**

NET ENERGY REQUIREMENT AS SUPPLIED TO PROCESS: 26,124 MM BTU/D *OR* 26.1 MM BTU/TON Al_2O_3

Table 4-6-2 (Sheet 1 of 5)

Alumina from Alunite via Reduction Roasting — Modified Bayer Processing Material Balance

1,000 TON/D Al_2O_3

Process Stream	1	2	3	4		6	7	8	9	10	11	12
Component												
Al_2O_3	788	788	785	798		1130	1161	1161	2629	2498	2479	1011
SiO_2	4483	4483	4465	4438		4394	4394	4394	4394	22		
Fe_2O_3	280	280	278	276		273	273	273	273			
$Al_2(SO_4)_3$	1320	1320	1314	1246		104						
K_2SO_4	671	671	668	664		657	2543	7	7	7		
Na_2SO_4	30	30	30	30		30	980					
KOH							2	1	1			
$NaOH$									2773	2713	2683	10
H_2O	417	417	416	17		12	13334	1031	17642	21145	21386	685
SO_2												
SO_3												
H_2SO_4												
O_2												
H_2												
CO												
CO_2												
N_2												
CaO												
Coal				85		88	88	88	88			
Fuel Oil												
Total	7989	7989	7956	7554		6688	22775	6955	27807	26385	26548	1706

All units are in short tons per day.

Table 4-6-2 (Sheet 2 of 5)

Alumina from Alunite via Reduction Roasting — Modified Bayer Processing Material Balance

Process Stream	13	14	15	16	17	18	19	20	21	22	23	24
Component												
Al_2O_3	1000	131	19		1468	1468	1468					
SiO_2		4372	22									
Fe_2O_3		273										
$Al_2(SO_4)_3$												
K_2SO_4			7									
Na_2SO_4												
KOH		1										
NaOH	10	60	30		2673	2673	2773	100				
H_2O		7106	44	600	21301	16511	16611	100		10609	285	
SO_2												
SO_3												
H_2SO_4												
O_2												668
H_2												
CO												
CO_2												
N_2												2216
CaO			23								23	
Coal		88										
Fuel Oil												
Total	1010	12031	145	600	25442	20652	20852	200		10609	308	2884

Table 4-6-2 (Sheet 3 of 5)

Alumina from Alunite via Reduction Roasting — Modified Bayer Processing Material Balance

Process Stream	25	26	27	28	29	30	31	32	33	34	35	36
Component												
Al_2O_3		11										
SiO_2												
Fe_2O_3												
$Al_2(SO_4)_3$												
K_2SO_4					2536	2536	1728	741	731	67		
Na_2SO_4					980	980	950			30		
KOH					1	1				1		
NaOH												
H_2O		877	4790	1545	13848	12716	12122	124	25	470	1132	
SO_2		5										
SO_3												
H_2SO_4												
O_2		34										
H_2												
CO												
CO_2		637										
N_2		2216										
CaO												
Coal												23
Fuel Oil	200											
Total	200	3780	4790	1545	17365	16233	14800	865	756	568	1132	23

Table 4-6-2 (Sheet 4 of 5)

Alumina from Alunite via Reduction Roasting — Modified Bayer Processing Material Balance

Process Stream	37	38	39	40	41	42	43	44	45	46	47	48
Component												
Al_2O_3				8								
SiO_2				44								
Fe_2O_3				3								
$Al_2(SO_4)_3$				14								
K_2SO_4		10		7								
Na_2SO_4												
KOH												
NaOH												
H_2O		99	14	202	282	259					96	355
SO_2				667	662	657	657	4		4		
SO_3								816				
H_2SO_4											4721	4721
O_2	6309			6267	6267	6267	6267	6887	180	6887		
H_2												
CO												
CO_2												
N_2									603			
CaO												
Coal												
Fuel Oil												
Total	6309	109	14	7212	7211	7183	6924	7707	783	6891	4817	5076

Table 4-6-2 (Sheet 5 of 5)

Alumina from Alunite via Reduction Roasting — Modified Bayer Processing Material Balance

Process Stream	49	50	51	52	53	54	55	56	57	58	59	
Component												
Al_2O_3					8			5	3			
SiO_2					44			27	18			
Fe_2O_3					3			2	2			
$Al_2(SO_4)_3$					14			9	6			
K_2SO_4					7			4	3			
Na_2SO_4												
KOH										104		
NaOH												
H_2O	280	75	23	1896	1816			399	1	1183	129	
SO_2			5		5			41				
SO_3												
H_2SO_4	3721	1000										
O_2						1674		7847				
H_2												
CO												
CO_2												
N_2						5603						
CaO												
Coal							655					
Fuel Oil												
Total	4001	1075	28	1896	1897	7277	655	8334	33	1287	129	

4.6.8 Equipment List

ALUMINA FROM ALUNITE PROCESS

Ore Preparation Area

Truck dump hopper
Apron feeders
Vibrating grizzly feed conveyor
Vibrating grizzly
Jaw crusher
Stockpile conveyor and stacker/reclaimer
Water spray system
Reclaim hopper
Reclaim apron feeder
Surge bin to screening conveyor
Surge bins
Vibrating screens
Secondary crusher
Fine bin feed conveyor
Fine ore bin
Fine ore weigh feeders
Rod mill feed conveyors and hoppers
Rod mill system
Ground ore conveyor
Ground ore silo
Ore drying feed conveyor
Ore drying screw feeder
Ore drying/roasting system
Baghouse - ore drying dust
Roasted ore conveyor
Ore handling dust collection system

Sulfuric Acid Manufacturing Area

Sulfuric acid manufacturing plant
Sulfuric acid storage tank

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EQUIPMENT LIST (Cont)

Leaching, Thickening and Filtration Area

Roasted ore surge bin
Leaching feed weighfeeder
Leaching feed conveyor
Leach tanks
Leach pumps
Leach tank agitators
45% KOH storage tank
45% KOH pumps
Leached ore thickener tanks
Leached ore thickeners rakes
Leached ore thickener underflow pumps
Leached ore thickener overflow pumps
Horizontal vacuum pan filters with scroll discharge
Wet leached ore conveyor
Pan filter mother liquor surge tank
Pan filter mother liquor pumps
Sand filters
K_2SO_4 filtrate tanks
K_2SO_4 filtrate transfer pumps

K_2SO_4 Crystallization, Centrifuging, Drying and Granulation Area

K_2SO_4 evaporative crystallizer system
K_2SO_4 crystallizer hotwell
K_2SO_4 crystallizer hotwell pumps
K_2SO_4 thickener
K_2SO_4 recycle pump tank
K_2SO_4 thickener pumps
K_2SO_4 recycle tank underflow pumps
K_2SO_4 recycle tank overflow bleed pumps
K_2SO_4 cyclones
K_2SO_4 centrifuges
K_2SO_4 centrate mother liquor tank
K_2SO_4 centrate pumps
K_2SO_4 conveyor
K_2SO_4 rotary dryer
K_2SO_4 rotary dryer cyclones

EQUIPMENT LIST (Cont)

K_2SO_4 rotary dryer baghouse
K_2SO_4 rotary dryer pneumatic conveyors
K_2SO_4 rotary dryer apron feeder
K_2SO_4 rotary dryer bucket conveyor
Fine K_2SO_4 storage bin
Fine K_2SO_4 bin conveyor
Fine K_2SO_4 bucket elevator
K_2SO_4 compacting mill
K_2SO_4 flakes belt conveyor
K_2SO_4 flakes bucket elevator
K_2SO_4 granulating mill
K_2SO_4 granules vibrating screen
K_2SO_4 granules rejects conveyor
K_2SO_4 granules accepts conveyor
K_2SO_4 granules rotary steam dryer
K_2SO_4 product apron feeder
K_2SO_4 product bucket elevator
K_2SO_4 product storage
K_2SO_4 dust collection system and baghouse
K_2SO_4 pneumatic conveyors

NaOH Digestion, Sand Settling, Washing and Clarification Area

Wet cake surge bin
Wet cake weigh feeder
Caustic digesters
Caustic digester agitators
Caustic digester pumps
Sand settler tanks
Sand settler rakes
Sand settler underflow pumps
Sand settler overflow pumps
Sand washer tanks
Sand washer rakes
Sand washer underflow pumps
Sand washer overflow pumps
Reslurry sand tanks
Reslurry sand pumps
Sand washer overflow transfer pumps
Desilicator reactors

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EQUIPMENT LIST (Cont)

Desilicator reactor agitators
Desilicator flash tanks
Desilicator heat exchangers
Desilicator flash tank transfer pumps
Desilicator heat exchanger condensate pumps
DSP cyclones
DSP pump tank
Coarse DSP slurry pump
DSP seed slurry thickeners
DSP seed slurry thickener rakes
DSP seed slurry thickener underflow pumps
DSP seed slurry thickener overflow pumps
Pressure filters, repulpers and sluice
Pressure filters vibrating screen
Press cake relay tank
DSP cake pump
Filtrate tank
Filtrate pumps

Starch Prep, Filter and Preparation Area

Sump relay tank
Sump relay tank agitator
Sump relay pumps
Wash water storage tank
Wash water pumps
Wash water relay tank
Wash water relay pumps
Dry starch bin
Dry starch bin baghouse and pneumatic conveyor
Dry starch weigh feeder
Starch mixing tank
Starch mixing tank agitator
Starch mixing overflow tank
Starch slurry transfer pump
Starch slurry storage tanks
Starch slurry tank agitators
Starch slurry pumps
Dilute caustic tanks
Dilute caustic tank agitators

EQUIPMENT LIST (Cont)

Dilute caustic tank pumps
Prepared starch storage tank
Prepared starch pumps
Lime storage silo
Lime weigh feeder
Lime screw conveyor
Lime slaker
Lime slurry tank
Lime slurry pumps
Filter aid tank
Filter aid tank agitator
Filter aid pumps
Lime pneumatic conveyor

Caustic Heat Interchange, Precipitation and Evaporation Area

Caustic stream heat interchange system
Heat interchange Hotwell
Heat interchange Hotwell sump pumps
Precipitation fill tanks
Precipitation fill pumps
Precipitators
Precipitator agitators
Precipitator air lifts
Mid stage flash tanks
Precipitation flash tanks transfer pumps
Primary feed tank
Primary feed tank agitator
Primary thickener feed pumps
Evaporation test tank
Evaporator feed pumps
Spent caustic evaporation system
Spent caustic evaporator product pumps
Spent caustic evaporator Hotwell
Evaporator Hotwell sump pumps
Digestion test tank
Spent liquor pumps
Evaporator transfer pumps
Caustic evaporator condensate pumps
Caustic storage tank

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EQUIPMENT LIST (Cont)

Caustic pumps
Caustic dilution tank
Dilute caustic pumps
Sump relay tank
Sump relay pumps
Sulfuric acid tank
Sulfuric acid pumps
Sulfuric acid dilution tank
Dilute sulfuric acid pumps
Sulfuric acid neutralization tank
Sulfuric acid neutralization pumps
Condensate tank
Condensate pumps
Fuel oil storage tanks

Product Thickening, Calcination and Storage Area

Primary thickeners
Primary thickener underflow pumps
Secondary thickeners
Secondary thickener underflow pumps
Tertiary thickeners
Tertiary thickeners rakes
Tertiary thickener underflow pumps
Tertiary thickener overflow pumps
Primary thickener wash tank
Primary thickener wash pumps
Primary thickener wash tank inlet screen
Secondary thickener surge tank
Secondary thickener surge pumps
Tertiary thickener seed storage tank
Tertiary thickener seed pumps
Wash liquor tanks
Wash liquor pumps
Secondary thickener surge tank agitator
Hydrate tanks
Hydrate pumps
Hydrate tank overflow pumps
Slurry density tanks
Slurry density pumps

EQUIPMENT LIST (Cont)

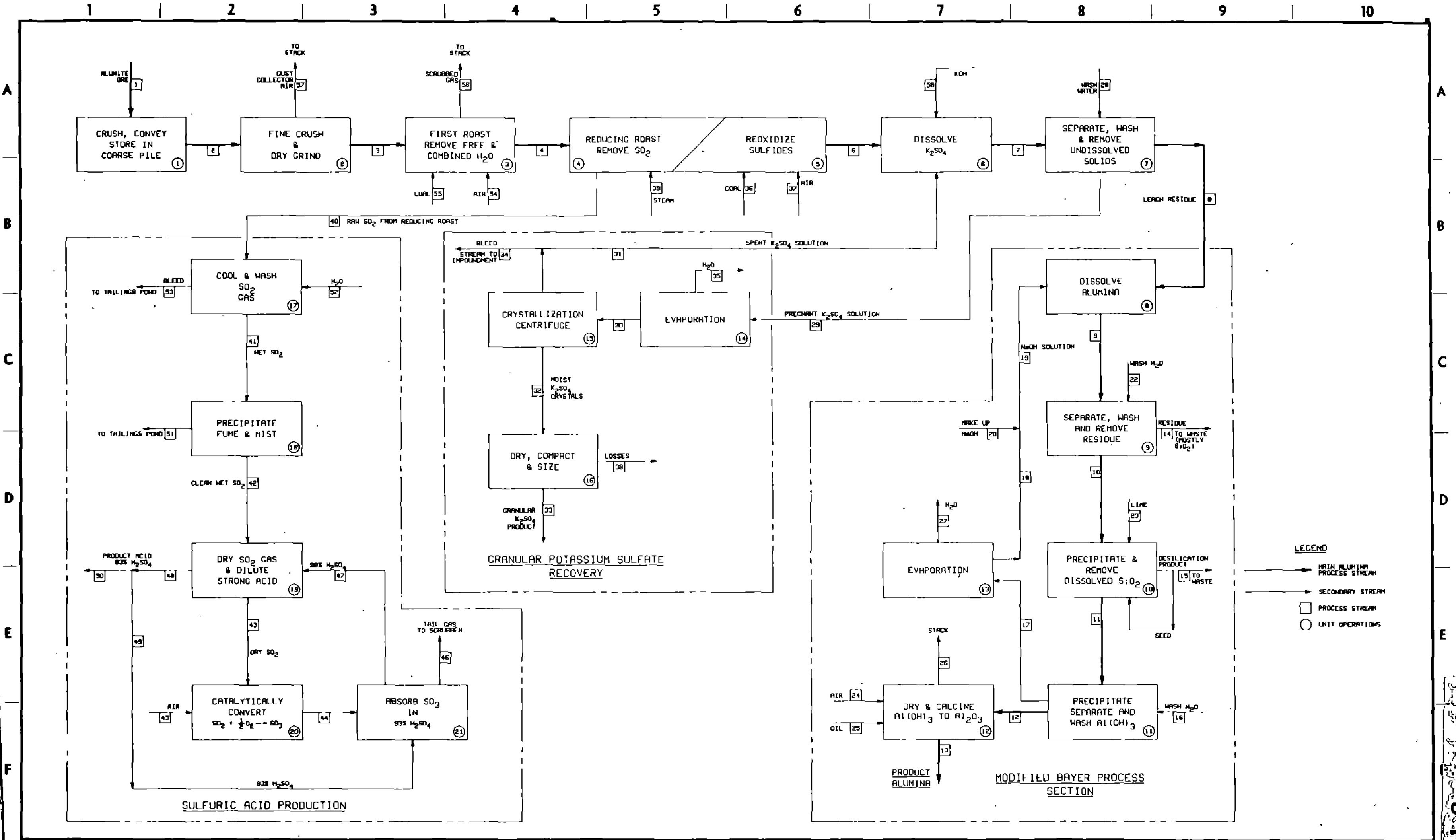
Hydrate filters
Filtrate receiver
Filtrate pumps
Wash water receiver
Wash water pumps
Vacuum pumps
Kiln feed conveyor
Rotary kilns
Rotary coolers
Fluo-solids coolers
Alumina conveyor
Dust cyclones
Electrostatic precipitator
Alumina silo

Major Dust Control Equipment

Ore drying/roasting gas scrubber system
Alumina kiln gas scrubbing system
Sulfuric acid plant tail gas scrubber
Boiler stack gas scrubber system

Utilities

Steam plant and auxiliary systems
Cooling towers and auxiliary systems



NO	DATE	REVISION	BY	CHK	APP	APP

NOTES

FOR INFORMATION ON PROCESS STREAM FLOWS SEE TABLE 4-6-II

FOR INFORMATION ON HEAT STEAM & COOLING WATER REQUIREMENTS SEE TABLE 4-6-I

DESCRIPTION	COST ACCOUNT

WHEN REVERSED BY THIS DRAWING CHANGE TO COST ACCOUNT ABOVE

CONSTRUCTION APPROVAL

APPROVAL	DATE	SCALE:	DATE
		DESIGNED BY	
		DRAWN BY ADS	
		CHECKED BY	
		APPROVED BY	
		APPROVED BY	

PROFESSIONAL SEAL

KAISER ENGINEERS

ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN
U.S. DEPARTMENT OF THE INTERIOR — BUREAU OF MINES — CONTRACT NO. J0265048

ALUMINA, SULFURIC ACID
AND
POTASSIUM SULFATE FROM ALUNITE

JOB No. 76161-001 FIGURE NO. 4-6-2 REVISION B-0

-248-

NOT REPRODUCIBLE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions to be drawn from this study are as follows:

(1) The HCl/Clay process using HCl gas-induced crystallization has the lowest operating and capital costs of the six processes studied. The operating costs can probably be reduced further by the recovery and use of waste heat and the conversion of clay calcination to a coal-fired fluid bed mode.

The principal area of the process that must be developed is the indirectly fired, $AlCl_3 \cdot 6H_2O$ decomposition system.

(2) The HCl/Clay process based on evaporative crystallization ranks second. It has the second lowest capital cost and the third lowest operating cost. It is similar in many ways to the top-ranked process except for the use of evaporative crystallization and direct-fired decomposition of the $AlCl_3 \cdot 6H_2O$. Operating costs can probably be reduced by the recovery of waste heat and the conversion of clay calcination to a coal-fired fluid bed mode.

(3) The Alunite process ranks number three. Although operating costs are the second lowest of the group, the capital cost is high, due in part to the need for H_2SO_4 and K_2SO_4 recovery equipment.

Although this process ranks third economically it is unlikely that it can be widely used by the aluminum industry because of the limited market for the large amounts of by-products which must be produced.

(4) The Anorthosite, Sulfurous Acid and Nitric Acid processes have very similar overall costs. They would be ranked an equal fourth.

Particular comments applying to each process are as follows:

a. The Anorthosite process capital and operating costs are both high relative to the base case. There are a large number of process steps resulting in high equipment costs plus an energy-intensive sintering step which adds significantly to the operating cost.

b. The Sulfurous Acid process has the highest capital cost in the group due to the large amount of equipment required for the long leach time, the two autoclaving steps, and the modified Bayer process. The process also has an environmental problem in that no method has yet been devised for the satisfactory disposal of the large waste filtrate stream from the filtration of the crude trihydrate in the sulfurous acid section of the process.

c. The Nitric Acid process has the highest operating costs of the six processes considered, and the capital costs rank third highest.

The operating costs can probably be reduced by the recovery and use of waste heat and the conversion clay calcination to a coal-fired fluid bed mode.

(5) Based on the above conclusions the HCl process using HCl gas induced crystallization and the HCl process using evaporative crystallization are recommended for further study in Task 2.

APPENDIX

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1. Alkaline Processes
2. Alunite
3. Sulfurous Acid
4. Nitric Acid
5. HCl Processing
6. General
7. HCl Properties

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