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**16. Abstract (Limit: 200 words)**
This study compares two nonbauxitic alumina processes with the objective of recommending the single most promising method for producing cell-grade alumina. The comparisons cover both technical and economic aspects of alumina process plants of a commercial size in the United States. The two processes (nitric acid clay and hydrochloric acid clay using HCl gas-induced crystallization) considered in this study were selected by the Bureau of Mines on the basis of factors reported in a previously issued study comparing six nonbauxitic alumina processes. 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 which show that the hydrochloric acid clay (HCl gas-induced crystallization) process is the more promising method to produce cell-grade alumina from nonbauxitic sources.

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# ALUMINA PROCESS FEASIBILITY STUDY AND PRELIMINARY PILOT PLANT DESIGN

## Task 2 Final Report: Comparison of Two Processes

FEBRUARY 1978

## 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

KAISER ENGINEERS

# 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 September, 1977 to February, 1978. This report was submitted by the authors in February, 1978. The report contains no patentable features.

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# 1. INTRODUCTION

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 29 months.

The first of the three task reports was issued in September, 1977. The objective of the first task was to reduce the number of candidate processes from six to two. The six processes 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 and other considerations, the Bureau of Mines selected the Clay/Nitric Acid and Clay/Hydrochloric Acid (Gas-induced Crystallization) processes and directed Kaiser Engineers to further study these two processes in the second task.

Thus, this report covers the second of the three tasks: Task 2. The objective of the task is to recommend to the Bureau of Mines the process technology of the two selected that has the greater potential for supplying cell-grade alumina from kaolinic clay. The method used to reach the objective of Task 2 requires the expansion and refinement of technical and economic factors considered in the previous task, which will allow a more detailed comparison of the two processes to be made. This refinement has caused some minor changes in the two processes. Based on the data and recommendations presented in this report, the Bureau of Mines will select the process to be considered in Task 3 of this contract. Task 3 will cover the preliminary design of a pilot plant in the range of 10 to 50 ton/d capacity.

The basic technical work for this study is supported by the miniplant program carried out by the Bureau of Mines on a cooperative, cost-sharing arrangement between several aluminum producers and the Bureau of Mines.

# 2. TECHNICAL AND ECONOMIC COMPARISON

## 2.1 TECHNICAL COMPARISON OF THE TWO PROCESSES

Following is a summarized technical comparison of the two 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 Leaching Acid

Nitric acid is monovalent with a molecular weight of 63.02, and costs approximately $125/ton on a 100% basis. Hydrochloric acid is also monovalent with a molecular weight of 36.46 and presently costs approximately $110 on a 100% basis. Both acids are chemically very aggressive reagents and both produce very soluble metal salts.

Although it is difficult to predict the future, we can expect the cost of $NH_3$, a major element in the cost of makeup $HNO_3$, to increase in coming years as the feedstock for $NH_3$ manufacture is shifted from natural gas to coal. The raw material sources and technology for the manufacture of HCl are expected to remain substantially unchanged during the foreseeable future, with the result that the cost of makeup HCl is expected to increase at the approximate general rate of inflation.

### 2.1.2 Chemical Stability

An unfortunate chemical characteristic of the nitrate group is that it is not completely stable at all temperatures required in a cyclic process for the extraction of alumina from clay, but tends to some extent to decompose in a complex series of equilibria to nitrogen oxides. These equilibria shift with increasing temperatures in a direction favoring the oxides containing lesser amounts of oxygen. Furthermore, all of the gaseous oxides of nitrogen are thermodynamically unstable with respect to the elements at all temperatures of interest in the extraction of alumina from clay. The rate of decomposition to the elements is very slow at temperatures employed in the extraction of alumina from clay, but any condition which might catalyze the decomposition could cause substantial loss of nitrogen by decomposition to elemental $N_2$, an essentially irrecoverable form. Some decomposition will inevitably occur. The process designer in a nitrate system must therefore provide, in addition to condensers for the bulk of the recycling acid, equipment for reconstituting oxides of nitrogen to acid. He must, in thermal decomposition, work at the lowest possible temperatures and strive to avoid the existence of any condition which would catalyze the decomposition of nitrogen oxides to $N_2$ and $O_2$.

Another consequence of the chemical nature of the nitrate group is that it may oxidize small amounts of chlorides inadvertently introduced into a cyclic process to either NOCl or $Cl_2$, with consequent severe corrosion problems in regard to metallic materials of construction.

Hydrochloric acid, in contrast, is completely stable under conditions encountered in the extractive process. It may be recovered by simple absorption/condensation, a process greatly facilitated by the very low equilibrium partial pressure of HCl over water solutions containing small percentages of HCl.

2.1.3 Iron Removal

The nitric acid extraction process, employing stoichiometric quantities of nitric acid extracts approximately 67% of the iron content of the clay, as does hydrochloric acid. Iron is removed by solvent extraction and the organic extractant regenerated in the case of both acid systems, but the chemistry is quite different. Two washings of the organic extractant are required in the nitrate system, and the end products are a waste $FeSO_4$ sludge and a waste dilute solution bearing both $Cl^-$ and $NO_3^-$. Utilization or disposal of the $FeSO_4$ sludge and the large volume of waste dilute wash solution containing both $Cl^-$ and $NO_3^-$ are at present unsolved problems. Losses of $Al^{+++}$, $NO_3^-$, and organic are incurred. Great care must be taken to assure that chloride, which is a necessary reagent in organic regeneration, is not inadvertently introduced into the primary liquor.

Iron removal in the chloride system, in contrast, requires no separate washing of the organic phase. $Al^{+++}$, $Cl^-$, and organic losses in the operation are essentially zero because the dilute $FeCl_3$ extract is reacted with calcined clay to reject iron as $Fe_2O_3$ while solubilizing $Al_2O_3$ from the clay as $AlCl_3$. The resulting dilute $AlCl_3$ returns to the process. Iron removal in hydrochloric acid extraction, as a result of development of the present removal method, has become a relatively simple and inexpensive operation.

2.1.4 Crystallization

The amount of solids to be handled per unit alumina in the nitrate system is 1.55 times the amount as chloride, requiring more effective washing to reach the same impurity level in the product alumina. Dissolved impurities entering crystallization in the nitrate system are concentrated by a factor of up to 10 during evaporation and the withdrawal of $H_2O$ entering into the formation of crystalline $Al(NO_3)_3.9H_2O$. In the HCl-induced $AlCl_3.6H_2O$ crystallization the increase in impurity concentration is by a factor of $< 2$, and the solubility of certain impurities will increase as the HCl concentration increases during crystallization. $Al(NO_3)_3.9H_2O$ has a greater solubility in condensed $HNO_3$ which might be used wash liquid than does $AlCl_3.6H_2O$ in 35% HCl.

Optimization of the crystallization section will require extensive further study regardless of which acid is used as the alumina extractant.

2.1.5 Energy Requirements

Aluminum nitrate crystallizes under all known practical conditions as $Al(NO_3)_3 \cdot 9H_2O$, whereas the chloride crystallizes as $AlCl_3 \cdot 6H_2O$. The heat of reaction to produce a unit of alumina by thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ is almost 50% greater than for the decomposition of $AlCl_3 \cdot 6H_2O$.

All of the water in which the $Al(NO_3)_3$ is dissolved when it leaves the leaching operation is subsequently vaporized, either in the evaporator or in thermal decomposition. When hydrochloric acid is used as the extractant and HCl gas is employed to induce crystallization, the water content of the $AlCl_3 \cdot 6H_2O$ is of course vaporized in thermal decomposition but the major part of the water in which the $AlCl_3$ is dissolved upon completion of leaching, recyles back to leaching without being vaporized. This fact, together with the thermal decomposition of a hexa- rather than a nonahydrate, are primarily responsible for a decreased capital requirement for heat transfer equipment and a lower overall process energy requirement for the hydrochloric acid process.

Heat may be recovered in both processes from the condensation of acid at a temperature high enough to be useful in certain process areas, such as evaporation. The quantity of such heat in the case of nitric acid extraction, however, is in excess of requirements in those process areas for which it is suited.

2.1.6 Thermal Decomposition

The larger energy requirement for the thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ as compared with the energy required for the decomposition of $AlCl_3 \cdot 6H_2O$ will result in a need for much greater heat transfer surface when decomposing $Al(NO_3)_3 \cdot 9H_2O$ under equivalent conditions. The need to operate at the lowest possible temperature to minimize nitrate decomposition to oxides of nitrogen and/or elemental $N_2$ is expected to result in operation with minimum temperature differences between the heat transfer surfaces and the bed solids, further increasing the required heat transfer surface along with decomposer volume and fluidizing steam requirements because of increased solids residence time in the decomposer.

$Al(NO_3)_3 \cdot 9H_2O$ melts in its water of crystallization, whereas $AlCl_3 \cdot 6H_2O$ does not. Restrictions are thereby placed on technology employed for the decomposition of $Al(NO_3)_3 \cdot 9H_2O$ in that decomposer conditions must be arranged to provide existing particles within the bed with successive layers of fresh liquid hydrate in a manner that will result in instantaneous decomposition of the liquid layer to a solid without adjacent particles adhering to one another. Particles of a suitably controlled size distribution must then be continuously removed from the decomposer to retain the desired particle size distribution within the unit.

Decomposer product particle size in the chloride system may be determined by the size of crystals fed to decomposition, allowing for shrinkage and attrition during decomposition. The particle shape during and resulting from chloride decomposition will be less spherical and therefore disadvantageous as compared with $Al(NO_3)_3 \cdot 9H_2O$ decomposition. Attrition may be greater during decomposition in the chloride system than in the nitrate one. The technology of indirectly fired nitrate decomposition, despite its somewhat greater complexity, is at the present time at a higher state of development than the technology for the decomposition of $AlCl_3 \cdot 6H_2O$.

2.1.7 Product Quality

Both acid systems are believed capable of producing alumina meeting reduction grade standards for chemical purity, particle size distribution, loss on ignition, and specific surface, although it is anticipated some of the standards finally chosen may be different from those applied to Bayer process alumina. Meeting the tentatively established standard of less than 0.01% Cl will be costly in the case of chloride route alumina, although it is not yet known with certainty whether chloride must in reality be reduced to this very low value.

Special measures, if any, that may be required for the control of phosphate are not yet known for either acid process.

### 2.1.8 Materials of Construction

An apparent advantage of nitric acid as an extractant in the early years of acid process development was the availability of metals and alloys suitably corrosion resistant. However, none of the early processes operated on a large scale over an extended time period. Unfortunately, most water supplies available for large-scale manufacturing purposes contain some dissolved chlorides. The cost of removing this chloride by ion exchange or other technology would be high. There is also a possibility that chlorides could be introduced into the primary liquor stream by malfunctioning of the iron removal process section. The level of chloride sufficient to corrode stainless steels in the presence of nitrates is very low and could easily be reached in a large-scale cyclic process. The percentages of metallic oxide impurities allowed in reduction grade alumina have been reduced in recent years. If a low level of chlorides were present in the process liquor it is doubtful that extensive use as unlined tankage, piping, pumps, etc., of anything but the most highly corrosion resistant (costly) alloys could be made today in an alumina plant employing nitric acid as the extractant. It was in the past extremely difficult to find metallic materials of construction suitable for use in the aqueous side of a hydrochloric acid-based process, but today a reasonably wide choice of polymeric liner materials is available for use with this non-oxidizing acid. A more limited selection of oxidation-resistant polymers, particularly at elevated temperatures, is available for service in the nitrate-based process. Certain of the Hastelloys, Zr, Ti, and Ta either as solid materials or possibly as coatings, are available under selected conditions as heat transfer surfaces for service in either acid system, and graphite is of course available for aqueous hydrochloric acid service.

Metallic corrosion resistance in general is based upon the maintenance of an adherent, stable oxide film on the surface of the metal. Such a film is generally much easier to maintain on metallic surfaces operating above the dew point. Zr, Ti, and Ta as solid materials or possibly as coatings are therefore potential candidates as materials of construction for heat transfer surfaces in either acid system at intermediate temperatures down to the dew point. A selection of chromium-nickel alloys, and Al as a coating, are candidate materials for service at higher temperatures. It appears that mechanical abrasion of decomposer heat transfer surfaces need not be a serious problem in either acid system.

### 2.1.9 Environmental Control

Virtually total containment of all solid and liquid wastes as well as gaseous pollutants will be required of either acid process. Special precautions will have to be taken in any nitrate-based operation because of the toxicity of nitrates to make certain that no dissolved nitrate escapes to the environment, and even then, the operator of a nitrate-based process may be faced with the burden of proving that some nitrate found in the environment did not originate with the alumina operations.

The nitrate process also yields a dilute waste solution from solvent extraction containing $Cl^-$, $NO_3^-$, and organics. A satisfactory method of disposing of this solution has not yet been devised. The same is true of the substantial volume of acidic $FeSO_4$ sludge produced by treatment of the iron extract with $H_2SO_4$ in the nitric acid process.

There will inevitably be, in a nitrate-based process, some decomposition of nitrates to lower oxides of nitrogen. Complete recovery of these, due to their chemical nature, is extremely difficult. Scrubbing equipment and/or catalytic combustors is certain to be required.

Some residual nitrate will remain in product alumina exiting the decomposer in the nitrate process. Provision must be made, at an additional expense for energy, to convert this nitrate to elemental $N_2$ in a reducing calcination so as to avoid the possibility of a $NO_X$ emission problem at the reduction plant if product alumina containing nitrate was fed to the cells.

The chloride-based process rejects iron as $Fe_2O_3$ to the same tailings disposal as the acid insoluble silica. Soluble chlorides and any organic in the iron strip liquor are returned to the process by the countercurrent waste solids washing process. It is planned, as with the nitrate-based process, that tailings will be impounded. Water containing small residual amounts of dissolved solids accompanying the tailings will be returned to the process to the extent it can be recovered.

The only gaseous chloride-containing substance produced by decomposition in the chloride process, or tending to volatilize from aqueous solutions, is HCl. Virtually total control of HCl is essential for successful operation of the process, but achievement of control is facilitated because HCl is very rapidly soluble in $H_2O$ and exhibits extremely low equilibrium partial pressures below concentrations of about 10% HCl in the aqueous phase.

Chloride process alumina containing approximately .01% Cl is not expected to produce gaseous emissions of HCl when added to the reduction cells. If a decision is made to use an alumina containing amounts of $Cl^-$ high enough to produce HCl emissions in the reduction plants, these could be controlled by water scrubbing of the smelter exhaust gases.

Both acid processes are expected to require scrubbing equipment for the containment of oxides of sulfur generated by the burning of coal.

2.1.10 Process Control

The development of a process control technology is still in a rudimentary state for either the nitric or hydrochloric acid processes, but fundamental parameters exist in both cases which are expected to make possible the eventual development of a high degree of automation for either process.

2.1.10.1 Analytical Methods

X-ray spectrographic analysis has achieved a high state of development for the analysis of clays.

A wet chemical method of analysis well suited to the analysis of clays, particularly when it is desired to disregard minor mineralogical constituents of the clay which would not be solubilized in industrial processing, is digestion of small samples of the clay at moderate elevated temperature and pressure with hydrochloric acid in a Zr or Ta bomb. Complexing agents are available and analytical methods are well developed which permit accurate determination by simple titration of the free acid and of the aluminum in acidic chloride solutions. Complexometric and AAS methods previously developed for the analysis of bauxites and aluminas are available for determination of other minor constituent metal oxides. Other well-developed analytical methods are available for the determination of $PO_4^{\equiv}$ and $F^-$ in the acidic solutions derived from the clays.

Analytical methods for the rapid determination of small amounts of impurities in the product alumina have, of course, reached a high state of development throughout the aluminum industry.

2.1.10.2 Leaching

Solids metering devices for controlling the amount of calcined clay entering leaching are readily available. The concentration of either nitric or hydrochloric acid is customarily determined by its density, although in the case of recycling hydrochloric acid, a correction will be required due to the presence of recycling dissolved $AlCl_3$ and small amounts of impurity metal chlorides. The leaching reaction in the case of both acids is exothermic and there is a boiling point rise in the leach solution which is a function of both the free acid and dissolved salt concentrations. Important parameters in monitoring the leaching operation are therefore: the temperature in the leaching reactors, the density of the leach liquor, and possibly the rate of flow of reflux acid returning to the reactors, which is a measure of the excess heat of reaction in a given reactor.

2.1.10.3 Solid-Liquid Separation

A major concern in this process section is the washing effectiveness achieved prior to discharge of the acid insolubles to waste. Here it is expected that a combination of pH measurement and chloride measurement by specific ion electrode will make possible adequate control of dissolved solids. Slurry density is another parameter which should be measured.

2.1.10.4 Solvent Extraction

A prerequisite to solvent extraction is quantitative oxidation of $Fe^{++}$ to $Fe^{+++}$ by means of $Cl_2$ in the chloride system. Oxidation of all iron to $Fe^{+++}$ will occur during leaching when $HNO_3$ is the leaching acid. The course of this oxidation in the chloride system is best controlled, and more than a negligibly small excess of $Cl_2$ avoided, by measuring the oxidation potential of the solution continuously by means of a Pt electrode immersed in the solution leaving oxidation.

The $Fe^{+++}$ content of the solution entering solvent extraction may be continuously determined colorimetrically. It is probable that this measurement can be used as the basis of control to provide an excess of solvent to extraction so as to assure essentially complete extraction of $Fe^{+++}$. Determination of the best method of obtaining a proof analysis for very small amounts of $Fe^{+++}$ in the raffinate primary liquor, and for continuously monitoring $Fe^{+++}$ in the loaded and regenerated organic, will require further study in the case of either acid system.

2.1.10.5 Evaporation

The best method for monitoring the course of the evaporation in either the nitrate or chloride system will be continuous measurement of liquor density. It is possible that specific ion electrode measurements may be employed to monitor the concentrations of $Ca^{++}$ and $Mg^{++}$, using these to estimate $SO_4^{++}$, $F^-$, $PO_4^{\equiv}$, $Na^+$, and $K^+$. As an alternative or for verification, liquor samples may be withdrawn periodically, evaporated to dryness, the solids thermally decomposed, and the remaining alumina analyzed spectrographically or by other means to determine minor constituent oxides/salts present. Determination of the best way of analyzing for minor constituents in the liquor leaving evaporation will require some further study.

The presence of hydrochloric acid in vapors from evaporation may be effectively monitored by density measurement or, in the case of very dilute solutions, by the measurement of pH.

2.1.10.6 Crystallization

It is necessary in the chloride system, to measure and control the volume of HCl gas entering crystallization. Means for doing this are commercially available.

A straight-line relationship exists between dissolved HCl + $AlCl_3$ and density in the system HCl-$AlCl_3$-$H_2O$ over the range of concentration of interest in the crystallization process, and this parameter is of primary importance in the control of this process section.

Close control of temperature is necessary in the $AlCl_3 \cdot 6H_2O$ crystallization in order to control crystal properties. The formation of $AlCl_3 \cdot 6H_2O$ is slightly endothermic, however the solution of HCl gas required to cause crystallization is strongly exothermic, resulting in a substantial net heat release during crystallization. Existing technology available from vendors appears adequate to accomplish the required temperature control.

The $Al(NO_3)_3 \cdot 9H_2O$ crystallization is accomplished by cooling. Liquor density and temperature are the primary control parameters in this crystallization. Control technology available from vendors is believed adequate.

2.1.10.7 Crystal Washing

Good crystal washing is essential to securing satisfactory alumina product purity. The best way to monitor washing efficiency is expected to be analysis of used wash acid. Specific ion electrode techniques are expected to be adequate for this analysis, but will require some further study.

2.1.10.8 Thermal Decomposition

The best method of controlling the thermal decomposition of $AlCl_3 \cdot 6H_2O$ probably will be to control the heat input into decomposer stages along with, of course, the amount of fluidizing gas. Bed pressure drop, including its fluctuation, is a primary indicator of bed operation. Product alumina analyses can be made by established methods for minor constituent oxides. The determination of residual chloride may be made by a specific ion electrode method following dissolution of a sample in chloride-free caustic.

Control of an indirectly fired $Al(NO_3)_3 \cdot 9H_2O$ decomposer is also expected to be accomplished by control of the heat input and the amount of fluidizing gas. In the case of nitrate decomposition, a liquid is sprayed into the bed beneath its surface and droplets of this liquid must coat existing solid particles within the bed with only a small amount of liquid so that it almost instantaneously vaporizes without the solid particles tending to adhere to one another. Control of the bed operation is expected to be more difficult and critical.

2.1.10.9 Acid Recovery

The hydrochloric acid leaching-HCl induced crystallization process faces the requirement of supplying HCl gas to crystallization and receiving HCl gas plus $H_2O$ vapor from decomposition under conditions when the supply vs. demand may vary between 0 and 200%. There are several approaches to this problem which may be used in combination, but by supplying 20% acid to the absorber and increasing the heat rejection from the condenser-absorber, it should be possible to send an excess of HCl to storage in the form of 35-37% acid as may be required. Similarly, in the presence of a demand for HCl gas greater than the supply from decomposition, 35-37% acid may be withdrawn from storage and supplied to the absorber-condenser where heat can be supplied to strip HCl from it down to concentrations approaching 20%, the HCl gas going to process, and the stripped acid returning to storage. The key control parameters here are heat supply or removal, acid supply or removal, and temperature. It should be possible by means of a computer to continuously match the HCl gas required by the crystallizer to that produced by the condenser-absorber even though the requirement for, and the supply of, HCl vapor to the condenser/absorber may vary independently within wide limits.

The $HNO_3$ recovery system will comprise a condenser operating at controlled temperature to permit the recovery of waste heat, followed by additional equipment for reconstitution of oxides of nitrogen to nitric acid and finally for destruction of unrecoverable oxides to elemental $N_2$. Control parameters in the reconstitution and destruction equipment are not known at this time.

2.1.10.10 Bleed Stream Treatment

The nitrate system bleed stream treatment comprises evaporation, crystallization, and then thermal decomposition with the same control parameters as the primary liquor stream. Bleed stream treatment in the chloride system comprises three-component distillation with temperature, waste chloride recycle rate and concentration, and heat supply being the primary variables. The control and other process technology for this distillation has already been developed by at least two U.S. vendors.

## 2.2 ECONOMIC COMPARISON OF THE TWO PROCESSES

### 2.2.1 Capital Cost Comparison

The capital costs for the two processes under study are compared in table 3-2. The comparative costs are broken down into three basic areas: equipment costs, waste disposal costs, and working capital costs.

The waste disposal cost is slightly greater for the nitric acid process to provide for additional sealing of the mud impoundment area to prevent nitrates leaking into the subsoil.

The working capital is based on storing sufficient reagents, fuel, etc. for a specific number of days. The cost-per-day of these materials is considerably greater for the nitric acid process which results in a higher working capital cost.

A breakdown of the process equipment cost differences are shown in table 2-2.

A review of this table in the form of annotated comments follows:

(1) Clay preparation equipment costs essentially the same with minor difference due to system capacity difference.

(2) The difference of $\$1.8 \times 10^6$ in leaching and sand removal arises from the higher cost polymer lining in thickeners and settlers to resist oxidizing acid in the nitric acid process versus rubber lining for the HCl process.

(3) The iron removal system is more complex for the nitric acid process than the hydrochloric acid process. The nitric acid system requires two additional wash stages plus additional evaporation equipment over those required for the HCl process.

(4) There is essentially no difference in cost for evaporation, crystallization, and centrifugation systems.

(5) Preliminary estimates indicate that an expanded-bed system for aluminum chloride decomposition in a 500,000 ton/yr plant would cost about $13,000,000 less than a dense-bed system. On the basis that the probabilities for successful development of either dense or expanded-bed designs and incorporation in a future commercial alumina from clay plant are about the same, the cost estimate for the 500,000 ton/yr plant incorporates the less expensive system, i.e., an expanded-bed system.

However, if it was assumed that a dense-bed system was used, then the total cost of the HCl/clay plant would increase by $13,000,000 and the difference in cost between the two processes would be reduced from $104,000,000 to $91,000,000. With either system the cost difference between the two processes is large.

# TABLE 2-2

## EQUIPMENT COST COMPARISON BY PROCESS AREA NITRIC ACID/CLAY VS. HYDROCHLORIC ACID/CLAY 500,000 TON/YR CAPACITY

| Process Area | Additional Costs for $HNO_3$ Process: $ x $10^6$ | Comment* |
|---|---|---|
| **Equipment Purchase Costs** | | |
| Clay Preparation | 0.143 | 1 |
| Leaching, Thickening, Washing and Filtration | 1.786 | 2 |
| Solvent Extraction, Organic Regeneration, and $FeCl_3$ Solution Processing | 1.007 | 3 |
| Evaporation, Crystallization, and Centrifugation | 0.223 | 4 |
| Product Recovery including Decomposition and Calcination | 26.280 | 5 |
| Bleed Stream Processing | 4.705 | 6 |
| Acid Recovery | 2.740 | 7 |
| Steam Plant | 0.331 | 8 |
| Subtotal | 37.215 | |
| **Other Direct Costs** | | |
| Erection, Foundations, Structures, Piping, Electrical, Instrumentation, Painting, Miscellaneous | 47.447 | 9 |
| Indirect Costs | 19.315 | 10 |
| Total Capital Cost Difference | $103.977 | |

*See comments in section 2.2.1.

Equipment costs for aluminum nitrate decomposition are \$26.3 x $10^6$ higher than for aluminum chloride decomposition. Aluminum nitrate decomposition costs are based on 19 dense-bed fluidized decomposers and one high temperature calciner. The aluminum chloride decomposition is based on four expanded-bed fluidized decomposers and two high-temperature calciners. Aluminum nitrate requires more equipment since 70% more gas is evolved from aluminum nitrate and because lower gas velocities are required for dense-bed decomposers compared to expanded-bed units (2.5 fps vs 10 fps). Aluminum nitrate decomposition probably is not adaptable to an expanded bed decomposer since the feed is introduced as a liquid which is sprayed onto existing solid particles. Expanded beds have a non-uniform solids distribution which would not lend itself to this type of mechanism. Furthermore aluminum nitrate decomposition requires nearly double the amount of heating equipment due to the much larger process heat requirement (21.3 x $10^6$ Btu/ton $Al_2O_3$ VS. 12.2 x $10^6$ Btu/ton)

(6) Equipment costs for bleed stream treatment in the nitric acid process are \$4.7 x $10^6$ higher than in the hydrochloric acid process. In the nitric acid process, costly decomposers (See comment #5.) are required for aluminum nitrate contained in the bleed stream. In the hydrochloric acid process, no decomposers are required since residual $AlCl_3$ is minimal after crystallization.

(7) Acid recovery is \$2.7 x $10^6$ more expensive for the nitric acid process primarily due to the much higher acid-containing gas loads from aluminum nitrate decomposition compared to aluminum chloride decomposition.

(8) There is essentially no difference in cost for steam plant and cooling towers.

(9) These are factored costs based on equipment purchase cost.

(10) These are factored costs based on total direct cost.

### 2.2.2 Operating Cost Comparison

The operating costs for the two processes under study are compared in table 3-1.

(1) Ore Cost

This cost is slightly higher for the nitric acid process due to the slightly higher alumina losses in the waste streams from this process.

(2) Reagent Cost

Reagent costs are considerably higher for the nitric acid process due to the relatively high usage of nitric acid. The main losses of nitrate from the process are with the waste residue to impoundment and as non-condensable $NO_x$ and $N_2$ lost from the aluminum nitrate calcination system. For operating cost purposes it has been assumed that 3% of the nitrate fed to the decomposition system will be lost as non-condensable $NO_x$ or $N_2$. However, even if this nitrate loss were assumed to be zero the operating cost differential between the processes would only be reduced about $15 per ton which is not sufficient to affect the economic ranking between them.

(3) Utilities Cost

The cost of utilities represents approximately one third of the total operating costs for both processes. Thermal energy costs account for essentially all of the difference in utility costs between the two processes. The detailed heat requirements for each process are shown in table 2-1 and these requirements are used to calculate fuel costs. Process energy costs incorporating recovery of waste heat are $8.03/ton greater for the nitric acid process than the hydrochloric acid process.

Table 2-1 shows the largest single energy requirement is for fuel to effect product recovery by decomposition and calcination of the corresponding aluminum salt. The nitric acid process requires approximately 50% more energy to accomplish this step and this accounts for most of the energy cost differential between the processes.

Both processes use Dowtherm heat transfer systems to perform decomposition. A waste heat boiler has been provided which uses the heat in the Dowtherm boiler stack gas to provide substantial steam for use in both processes. In the nitric acid process, this steam is used to melt aluminum nitrate crystals

TABLE 2-1

# ALUMINA FROM CLAY PROCESSES HEAT REQUIREMENT COMPARISON (Units: $10^6$ Btu/ton $Al_2O_3$)

| | $HNO_3$ PROCESS | | HCl PROCESS | |
|---|---|---|---|---|
| | COAL FOR STEAM | FUEL | COAL FOR STEAM | FUEL |
| CLAY CALCINATION | | 4.9 | | 4.7 |
| EVAPORATION | 7.1 | – | 5.7 | – |
| PRODUCT RECOVERY | | | | |
| CRYSTAL MELTING | 2.0 | – | – | – |
| DECOMPOSITION | – | 21.3 | – | 12.2 |
| CALCINATION | – | .6* | – | 2.2* |
| WASTE HEAT | (15.8) | – | (5.7) | – |
| BLEED STREAM TREATMENT | | | | |
| EVAPORATION | .2 | – | .8 | – |
| HCL STRIPPING | – | – | .7 | – |
| DECOMPOSITION | – | 1.6 | – | .1 |
| IRON REMOVAL | | | | |
| CLAY DIGESTION | – | – | .2 | – |
| HCl DISTILLATION | 6.5 | – | – | – |
| **TOTALS** | 0 | 28.4 | 1.7 | 19.2 |
| **PROCESS TOTAL** | 28.4 | | 20.9 | |

*Fuel oil or natural gas necessary

prior to decomposition and to evaporate the bleed stream. In the hydrochloric acid process, this steam is used to preheat the liquor stream entering evaporation, thus providing about one third of the heat for evaporation.

Additional waste heat is recovered from the condensation of the acid/$H_2O$ vapors generated in the salt decomposition step. Condensation of nitric acid provides enough heat to evaporate the main process liquor stream prior to crystallization and to evaporate the spent HCl stream coming from solvent extraction.

Condensing HCl provides the balance of the heat required to evaporate the process liquor steam prior to $AlCl_3$ crystallization.

The table shows that for the nitric acid process, waste heat provides all of the heat which would normally be supplied by steam generated from coal or $15.8 \times 10^6$ Btu/ton for a savings of $19.75/ton. In the hydrochloric acid process, savings are $5.7 \times 10^6$ Btu/ton or $7.13/ton.

(4) Labor Costs

Labor costs for the nitric acid process are higher than the hydrochloric acid process for several reasons.

Operating and supervision personnel requirement are estimated to be about 8% higher for the nitric acid process due to the greater amount of equipment in the plant as evidenced by the higher capital cost for this process.

R & M labor is estimated as a percentage of the equipment cost which results in a higher charge for the nitric acid process due to its higher equipment cost.

(5) Supplies Cost

The cost of supplies for the nitric acid process is considerably higher than for the hydrochloric acid process. The two main reasons for the cost differential are:

(a) The R & M supplies cost is higher due to the higher capital investment in the nitric acid plant, and

(b) The additional costs for the HCl lost from the solvent extraction system and the sulfuric acid used to treat ferric chloride. These have no counterpart in the hydrochloric acid process.

(6) Other Cost

This cost category represents taxes and insurance which are higher for the nitric acid process due to the higher capital investment in the plant.

### 2.2.3 The Effect of Ore Quality Variations on Capital and Operating Costs

The basic process economics for the nitric acid/clay and the hydrochloric acid/clay processes were developed based on using a clay similar to that used in mini-plant operations. It is conceivable that a commercial plant could be built which would depend on a clay having a different analysis. In order to examine the economic impact of varying clay quality, a sensitivity analysis was performed for the three major clay quality variables. The variables studied were: 1) the effect of reducing clay alumina content by 20% from 36.5% to 29.2% on a dry clay basis, 2) the effect of doubling the clay iron content from 0.86% $Fe_2O_3$ to 1.72% $Fe_2O_3$ and 3) the effect of doubling the amount of "other" (mainly Ca, Mg, Na, K, Ti salts) impurities present in the clay from 2.7% to 5.4% on dry clay. The range of these variations was chosen somewhat arbitraily, but study of typical clay analyses for the Georgia clay belt indicates that there is a good probability that the clay quality available falls within the ranges chosen.

The effect of the above changes on capital and operating costs is shown in table 2-3. The table shows that the HCl/clay process costs are markedly less sensitive to changes in iron and soluble "other" impurities. The processes are nearly equal in their cost sensitivity to a lower alumina content clay with the HCl process having an advantage in capital costs and the $HNO_3$ process an advantage in operating costs.

A reduction in clay alumina is assumed to increase clay silica and therefore increase the amount of clay and residue which must be processed. The processes are both affected to the same extent by variations in clay alumina content since the processes use essentially the same methods and equipment for all operational steps from clay preparation through mud (or sand) removal. This is not the case for variations in iron and "other" impurity levels in the

## TABLE 2-3

### THE EFFECT OF ORE QUALITY VARIATIONS ON CAPITAL & OPERATING COSTS

| Ore Quality Variation | Additional Costs: $HNO_3$/Clay Capital[1] | $HNO_3$/Clay Operating[2] | HCl/Clay Capital[1] | HCl/Clay Operating[2] | Difference between HCl and $HNO_3$ processes Capital[1] | Difference Operating[2] |
|---|---|---|---|---|---|---|
| Reduce Clay Alumina Content by 20% from 36.5% to 29.2% $Al_2O_3$ on dry clay | 42.87 | 9.19 | 41.31 | 10.13 | 1.56 | (.94) |
| Double Clay Iron Content from 0.86% to 1.72% $Fe_2O_3$ on dry clay | 4.81 | 12.52 | 3.35 | 2.32 | 1.46 | 10.20 |
| Double Clay "Other" Impurities Content from 2.7% to 5.4% on dry clay | 8.79 | 2.88 | 1.96 | 1.05 | 6.83 | 1.83 |

1) Capital costs are shown as $10^6$ dollars for 500,000 ton/yr capacity.
2) Operating costs are shown as dollars per ton $Al_2O_3$ produced.

Note: All positive numbers represent additional costs due to the ore quality variation. Figures in brackets represent reduced costs.

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clay. In the nitric acid process, additional mixer-settlers are required to water wash the organic stripping solution. Furthermore, 17% HCl stripping liquor is required to regenerate the loaded organic solution compared to 0.1% HCl for the hydrochloric acid process. Both operating and capital costs are increased in the nitric acid process to provide for the use and recovery of this stripping liquor.

The system for rejection of "other" impurities is also more costly for the nitric acid process. The soluble fraction of these impurities which is dissolved in the leach step is removed from the process via the bleed stream. An increase in the amount of impurities proportionally increases the amount of equipment required to process the bleed stream. This adversely affects the nitric acid process capital costs to a greater extent than the hydrochloric acid process. Operating costs are affected since the nitric acid bleed stream processing requires an aluminum nitrate decomposition step with a corresponding heat requirement which is not necessary in the hydrochloric acid process.

# 3. TABLES FOR COST COMPARISONS

## 3.1 OPERATING COST COMPARISON TABLE 3-1

### 3.1.1 Method Used to Develop Operating Costs

Table 3.1 presents operating cost comparisons for the two processes considered. The comparative costs are presented as the difference, in cost per ton of alumina produced, between the $HNO_3$ 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 lower total operating cost per ton of product.

The operating costs are grouped into six cost elements. 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. The unit cost of clay is identical in both cases. Mine-to-plant haul distance is assumed to be five miles.

Each process is dependent on an acid 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. Material usages have been based on the process material balance. Freight effects are based on the assumption that clay process plants would be near Augusta, Georgia.

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 both 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 the same

TABLE 3-1

OPERATING COST COMPARISON
500,000 TON/YR $Al_2O_3$

| Operating Cost Difference, \$/Ton $Al_2O_3$ | $HNO_3$ | HCl Sparging* |
|---|---|---|
| Ore (Excluding Mining Capital) | .32 | Base Case |
| Reagents (Acids & Bases) | 21.50 | Base Case |
| Utilities (Oil, Coal, Power, Water) | 9.47 | Base Case |
| Labor (Operating, R & M, Supervision, Administration) | 4.49 | Base Case |
| Supplies (R & M, Operating, Processing) | 12.31 | Base Case |
| Other (Taxes and Insurance) | 2.50 | Base Case |
| Total Difference, \$/Ton $Al_2O_3$ | 50.59 | Base Case |

Note: Costs shown represent the difference between the two processes. 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

rate for both processes. 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 the processes arise from R & M materials which are based on capital cost.

The "Other" element represents taxes and insurance. It is calculated as a fixed percentage of capital for all processes.

The comparative total operating cost difference represents a totaling of the six elements of differential cost. These values represent the total additional cost of producing one ton of alumina for the HNO3 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 based on the required annual tonnage. Overburden removal is required for kaolin clay. 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 capital estimates include both mobile equipment and fixed facilities such as shops, utilities, roads, and fuel storage. The values shown in the capital cost table represent the difference in required mining cost 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 last half of 1977.

Values for process equipment represent the differences of installed equipment cost between the nitric acid process and the base case in dollars per annual ton. Other direct capital cost differences for foundations, structures, piping, utilities, electrical, etc., are developed from 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 exclude 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. The mined-out area created by ore removal has been assumed suitable for mud

TABLE 3-2

CAPITAL COST COMPARISON
500,000 Ton/Yr Plant

| Capital Cost Difference, $/Aton* | $HNO_3$ | HCl Sparging** |
|---|---|---|
| Mining Capital Difference | -0- | Base Case |
| Process Plant Capital Differences | | |
| Process Equipment | 73.78 | Base Case |
| Other Direct Capital (Foundations, Structures, Piping, Utilities, Electrical, etc.) | 95.55 | Base Case |
| Indirect Capital and Freight | 38.63 | Base Case |
| Waste Disposal Capital Difference | 3.00 | Base Case |
| Working Capital Difference | 2.83 | Base Case |
| Total Capital Cost Difference, $/Aton | 213.79 | Base Case |

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

disposal. 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. All items are charged at their cost of production or purchase.

# 4. APPRAISALS OF TWO PROCESSES

## 4.0 Raw Material Background: Clay

### 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 clay 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.

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## 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.

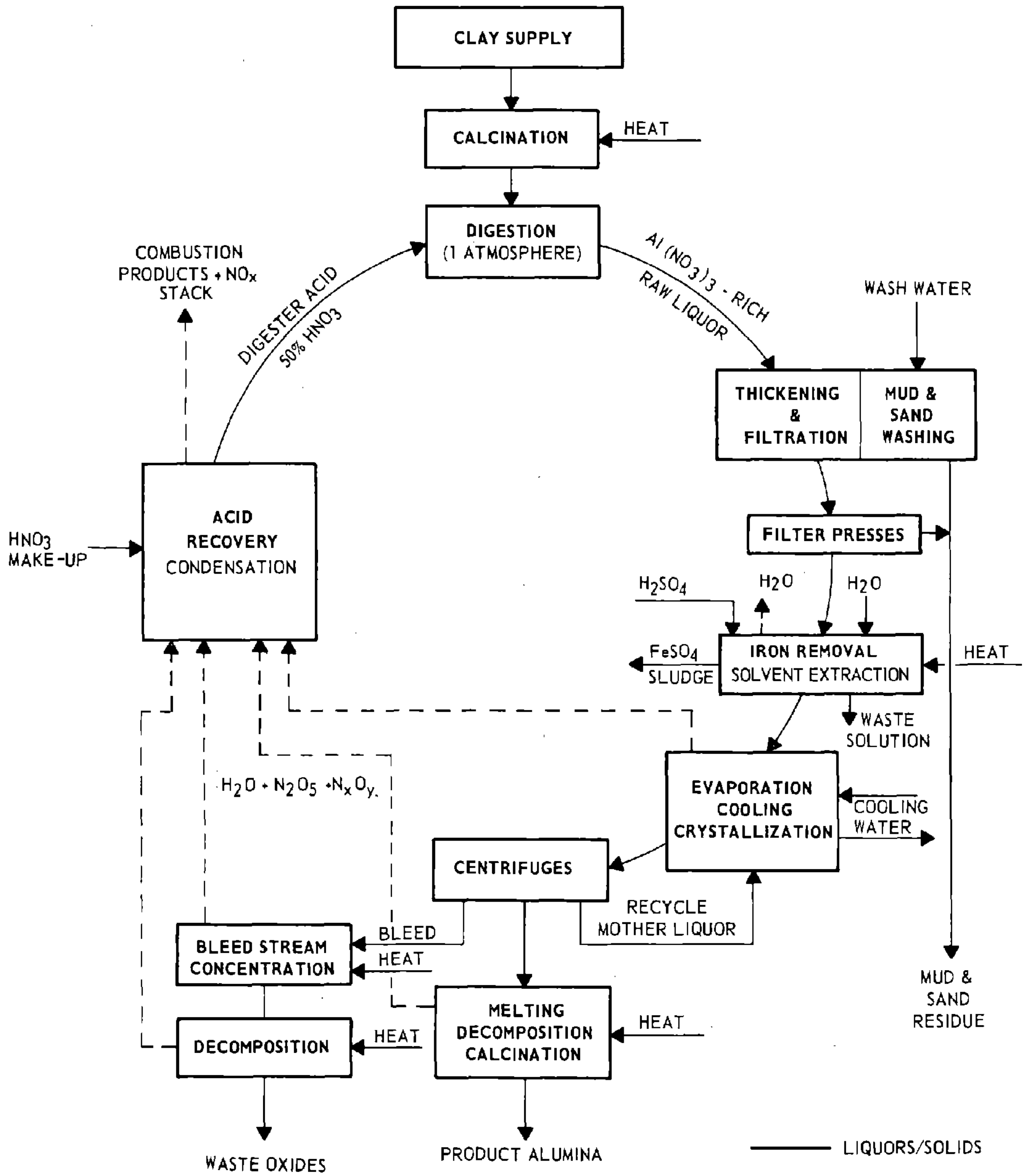
(7) Thermally decomposing the $Al(NO_3)_3 \cdot 9H_2O$ to obtain the product alumina.

(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 fuel requirement for the process is $28.4 \times 10^6$ Btu/ton alumina. 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.

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 when operating at industrial scale will be difficult.

Three 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 $FeSO_4$ sludge and chloride-bearing wash water from the solvent extraction system. These wastes cannot be expelled into the environment and cannot be impounded indefinitely in any region having a natural excess of precipitation over evaporation. These streams also constitute a significant nitrate loss.

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

(3) Information about the crystallization process similar to that required for hydrochloric acid-based extraction must be developed in order to determine much more accurately the size of crystallization equipment required for a demonstration plant, the size of the bleed stream, the proper crystal washing procedure and whether or not recrystallization will be necessary to meet final product alumina specifications.

In addition, solid-liquid separation and clay calcination would benefit from the availability of additional engineering design information. However, additional information on these process sections is not as critical as for the three above identified process sections.

### 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. Unfortunately, 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. It effectively dissolves the alumina content of calcined clay. The solubility of silica in nitric acid 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 180 g/l 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 $Al(NO_3)_3 \cdot 9H_2O$.

(7) Nitric acid and solutions of nitrates may be contained in equipment constructed of several different metals in the absence of chlorides. Heat transfer surfaces of several different alloys may be used in equipment for the purpose of decomposing $Al(NO_3)_3 \cdot 9H_2O$ because the metals are protected from corrosion by a developed thin, tightly adhering film of metal oxide.

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 amount 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 3776, 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 Engineering 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 are then 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 98% 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. Clay 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 1,200-1,500°F in order to render the clay suitably reactive to the leaching acid. The reaction is:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \longrightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \uparrow$$

$$\Delta H = 624 \text{ Btu/lb } Al_2O_3$$

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 removes 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.

The employment of fluidized solids techniques for carrying out the clay calcination is proposed on the basis of a report in the Russian literature and vendor information. It appears that this technique could offer the following:

(1) A significant reduction in thermal energy requirements in comparison with calcination in a rotary kiln.

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

(3) Possible capital savings in calciner cost.

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 of undesirable particle size with an attendant uncertain degree of calcination.

4.1.3.3 Leaching

The primary leaching reaction is:

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

$$\Delta H = 1505 \text{ Btu/lb } Al_2O_3$$

The technology for leaching is well developed. It is expected that calcined clay and a small stoichiometric excess of acid will be simultanesouly 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. Condensed $HNO_3$ and $H_2O$ will be returned to the leaching system. The non-condensable $NO_x$ are subsequently converted to $N_2$ in a catalytic burner.

It is expected that about 67% 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 $240^{\circ}$ -$250^{\circ}F$. 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 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 di-ethyl-hexyl phosphoric acid (DEHPA) 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.

The first water wash may be returned to the process by employing it as wash liquid in the waste residue washing system, thereby returning to the process some nitrate and organic that would otherwise constitute losses, while at the same time avoiding any need to find a means of disposing of this stream. The other two aqueous streams represent important losses of nitrate, organic extractant, and alumina occurring in combinations which cannot be discharged to the environment.

The iron-bearing, used HCl solution is first treated with $H_2SO_4$ and then evaporated to produce a waste $FeSO_4$ sludge to recover most of the HCl. It is unfortunate that conversion of the iron-bearing solution to dilute $AlCl_3$ by reaction with calcined clay cannot be used in the nitric acid extraction process because the $AlCl_3$ cannot be returned to the nitrate-based primary liquor stream.

The 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 chloride-bearing 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

Single-effect operation has been specified for the evaporation due to the use of low-temperature-availability reclaimed heat in this operation. 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.

It is planned that the evaporative process will be engineered to utilize heat recovered in the condensation of nitric acid vapors from decomposition to accomplish evaporation requirements.

4.1.3.7 Crystallization

The preceding vacuum evaporation yields a liquor which at temperatures lower than those prevailing in the evaporator is super-saturated with respect to aluminum nitrate. This liquor is cooled evaporatively in at least two stages of crystallization to prepare $Al(NO_3)_3 \cdot 9H_2O$. Reclaimed heat is also used as the energy source where further evaporation is necessary in this operation. The crystals are recovered by centrifuging and then may be washed with 50% nitric acid. The 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. 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 <u>Decomposition</u>

It is expected that $Al(NO_3)_3 \cdot 9H_2O$ crystals of requisite purity will melt 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 in stages 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 1,800°F to destroy the last traces of nitrate in the product alumina.

The idealized overall reaction for the decomposition is:

$$2Al(NO_3)_3 \cdot 9H_2O_{(1)} \rightarrow Al_2O_{3(c)} + 6HNO_{3(g)}\uparrow + 15H_2O_{(g)}\uparrow$$

$$\Delta H = 5{,}950 \text{ Btu/lb } Al_2O_3$$

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.

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

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

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

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

$$2NO \rightarrow N_2 + O_2$$

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

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 or in the presence of a catalyst.

$N_2O_5$, $NO_2$, 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.

Nitrate decomposition studies carried out by INEL did permit construction of a nitrogen balance. Independent calculations performed under this contract 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 available for another nitrate-alumina extraction process, employing a decomposition step 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 <u>Bleed Stream Treatment</u>

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 gross thermal energy requirements required by the process are $44.2 \times 10^6$ Btu/ton of alumina. However, $15.8 \times 10^6$ Btu per ton can be supplied by the recovery of heat from the process so that the heat which must be actually supplied to the process as fuel amounts to $28.4 \times 10^6$ Btu/ton. Details are shown in table 2-1.

Coal is used to fire the fluid bed clay calciners, and coal-fired Dowtherm boilers are used to supply heat for aluminum nitrate decomposition. Fuel oil is used directly to calcine alumina to prevent product contamination with ash.

A substantial amount of process heat, equivalent to $15.8 \times 10^6$ Btu/ton $Al_2O_3$ is normally supplied in the form of steam. It is anticipated that all of this heat can be recovered as waste heat from the condensation and decomposition sections of the process. A coal equivalent of $2.9 \times 10^6$ Btu/ton $Al_2O_3$ is available as steam generated in a waste heat boiler fired by the hot gases from the Dowtherm boiler stacks and the balance of the required heat ($12.9 \times 10^6$ Btu/ton $Al_2O_3$) is available from condensation of $HNO_3$ and $H_2O$ vapor evolved in aluminum nitrate decomposition.

Process heat requirements would be increased if impurities in the clay resulted in the need, either to increase the bleed stream, or to re-crystallize aluminum nitrate. The use of coal to calcine clay may not be feasible if a substantial part of the ash is soluble in nitric acid. Developmental testing is required.

### 4.1.5 Environmental Impact

The extraction of alumina from clay via nitric acid will require total impoundment of the waste solids 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 Materials of Construction

In a system using large amounts of nitric acid, a major concern is the corrosion resistance of containment materials. This is further complicated in systems where combinations of $HNO_3$-$H_2O$, metal chlorides, particulates, and other contaminants are present. Organic solvents used in iron removal from the pregnant liquor stream further limit material selection by complicating the corrosive environment. Although the stainless steel 300 series has been used successfully in handling various streams containing nitric acid, to build containment vessels out of these materials is costly. Continuing research, development, and investigative work with metals, ceramics, cements, conversion coatings, direct coatings, polymers, and fibre reinforced plastics (FRP) materials in a nitric acid environment should be carried out.

The effect of varying combinations of contaminants with the $HNO_3$ media at a wide range of flow rates, entrained particles, temperatures, and pressures is generally known, but will still require specific evaluation of actual operating situation and conditions.

#### 4.1.7.1 Candidate Materials

For the low temperature systems of the process more conventional material may be used. Typically, these include:

- Linings/coatings on steel such as:
  - Acid brick
  - Polymers - Kynar, Teflon, Saran, Polypropylene, Polyvinyl Chloride, etc.
- Steel Alloys
  - 300 series stainless
  - Precipitation hardenable nickel chrome

- Titanium and its alloys
- Fibre reinforced plastics (FRP)
- Impervious graphite compounds
- Ceramics and glass materials

The use and applicability of the above materials is dependent on conditions such as stream analyses, temperature, and particulate content. Generally, lined steel could be used for pipe, tank, and pressure vessels whereas the other solid materials can be used for pump impellers, valve internals and heat exchanger tubing. The metallic alloys can be used in most applications. The basis of selection would include the utilization of those materials having an adequate service life along with minimizing the contribution of harmful corrosion products to the product stream.

In those cases where coatings will be used in $HNO_3$ media, assurance of high coating quality and integrity is mandatory. Since some metals are dependent upon film formation for retardation of corrosion, dynamic testing programs utilizing process flow rates and typical particulate concentrations should be implemented.

As of this report date the more promising candidate materials for the lower temperature service would be:

$<180^{\circ}F$--polymeric-lined steel and series 300 stainless steels

$180^{\circ}F$ - $350^{\circ}F$--Kynar/Teflon over steel and series 300 stainless steels

$>350^{\circ}F$--Polymer-lined steel with castable refractory and acid brick lining

### 4.1.7.2 Process Area and Materials Review

Following is a general review of several process areas and the materials considered for fabrication of components.

(1) Atmospheric Leach

The calcined clay is leached with 50% nitric acid at atmospheric pressure. The resulting exothermic reaction at 240°F maintains the liquor in the leach tanks at the boiling point emitting $HNO_3$, $H_2O$, and $NO_x$ vapors.

Corrosive attack by the $HNO_3$ - $Al(NO_3)_3$ containing solution plus some abrasion due to silica are the concern in this system.

- Candidate Materials

- Leach Tanks: Carbon steel - polymeric contact lining plus acid resistant brick interfacing the leach liquid.

- Flash Tanks: Carbon steel - polymeric contact lining plus acid resistant brick.

- Condensers: Stainless steel type 304L

(2) Iron Removal

This system requires five operations as follows: iron extraction, nitrate washing, solvent regeneration, chloride washing, and HCl regeneration. In the iron extraction step, solvent is added to the liquor. The second step requires washing the unwashed loaded solvent with hot water. The next step is to regenerate the loaded solvent to convert the iron to the ferric chloride state by the addition of a 17% hydrochloric acid wash. In the fourth step, the chloride wastes are removed out of the organic solution by washing with hot water. In the final step, the spent HCl solution is evaporated in a reboiler, reacted with $H_2SO_4$ and the resulting waste neutralized.

Rubber materials and certain polymers experience early failure in the containment of this organic solvent even at this low-operating temperature of approximately 120°F.

- Candidate Materials

  Generally, FRP materials can be used to line the containment vessels throughout this system. Stainless steel alloys can be considered for exposed metal applications in the first two operations. In the third and fourth operations, titanium alloys may be used. The plastic materials used in the FRP layups would be selected on the basis of test results. Glass or ceramic-lined vessels and impervious graphite heat exchanger tubes may be used for HCl regeneration.

(3) Evaporation

The iron free pregnant liquor in the evaporative system will be at various low concentrations. For vessels where the operating temperatures are 150°F or less, Polyvinyl chloride liners may be used. When the operating temperatures are higher, the vessels may be constructed of stainless steel type 304L. For heat exchangers, stainless steel can be used for both shell and tubes.

(4) Crystallization/Centrifugation

The product stream from the evaporation process is cooled in the crystallization step to obtain an $Al(NO_3)_3 \cdot 9H_2O$ slurry of crystals and mother liquor. The crystals are separated from the mother liquor by centrifuging. Temperatures in these two steps are less than 200°F and stainless steel type 304L materials could be used. Abrasiveness of the crystals and slurry may prove to give a life limitation to certain pieces of equipment. This would require evaporation on an item-to-item basis dependent on product liquid and solids content. A corrosion resistant, precipitation hardenable nickel chrome steel may be used as an alternate for the centrifuge wear parts.

(5) Decomposition

Operating experience at INEL at Idaho Falls showed that 300 series stainless steels performed adequately with little or no corrosion occurring for extended periods and high temperatures. In the interest of cost reduction for large size commercial decomposers the vessels can be adequately designed using carbon or alloy steels lined with castable refractory plus high alumina refractories. A polymeric liner may be used to protect the steel shell, provided ample insulating lining and acid brick is installed to avoid damage to the polymeric lining due to high temperature exposure.

4.1.8 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 four in the last five 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.

(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. 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, but can be supplied by waste heat.

(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.

### 4.1.9 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:

| | % |
|---|---|
| $SiO_2$ | 46.4 |
| $Al_2O_3$ | 36.5 |
| L. O. I. | 13.54 |
| $TiO_2$ | 2.23 |
| $Fe_2O_3$ | 0.86 |
| MgO | 0.082 |
| CaO | 0.042 |
| $K_2O$ | 0.095 |
| $Na_2O$ | 0.046 |
| $SO_4^{=}$ | 0.10 |
| $P_2O_5$ | 0.069 |
| $F^-$ | 0.022 |
| Other | 0.04 |
| TOTAL | 100.0% |

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

(4) Powdered coal direct-fired fluidization is used in calcination of clay.

(5) There is a 1% dust loss (calcined basis) in clay calcination.

(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) 13.25% of "other" is solubilized in the leaching step.

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

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

(11) 1% of the soluble alumina leaving leaching section 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) Single effect evaporators are used for the concentration of the main aluminum nitrate solution and the bleed stream of aluminum nitrate when operating on reclaimed heat.

(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 4-1-2 (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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | *amb. | amb. | 250 | 150 | 150 | 140 | 135 | 130 | 120 | 160 | 160 |
| **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 | 6349 | 6335 | 9437 | 6242 |
| Other | 84 | 84 | 1 | 83 | 83 | 83 | 11 | 10 | 10 | 130 | 130 |
| $HNO_3$ | | | | | | 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 | 11006 | 10990 | 10925 | 19135 | 19135 |

All units are in short tons per day
*amb.: ambient

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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 160 | 200 | 500 | 500 | 150 | 160 | 160 | 160 | 120 | 200 | 150 |
| **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 | 120 | 9 | 9 | | 9 | 9 |
| $HNO_3$ | 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 | 10920 | 818 | 718 | 100 | 718 | 45 |

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 | | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 500 | | 115 | 115 | 180 | 125 | 125 | 125 | 1060 | amb. | 120 |
| **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 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 135 | 135 | 120 | amb. | 130 | amb. | 120 | 120 | 120 | 120 |
| **Component** | | | | | | | | | | |
| $Al_2O_3$ | 56 | | 56 | | | | | | | |
| $Al(NO_3)_3$ | 1479 | 1435 | 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 | | | | | | | | | | |
| $H_2O$ | 2054 | 3668 | 3718 | 9 | 10 | | | 3481 | 3481 | |
| Other | 72 | | 72 | | 1 | | | | | |
| $HNO_3$ | 86 | 84 | 19 | | | | | | 14 | |
| $N_2O_5$ | | | | | | | | | | |
| HCl | | | | | | | | | | |
| Organic | | | | | | 1 | 2811 | | | 2811 |
| $CO_2$ | | | | | | | | | | |
| $O_2$ | | | | | | | | | | |
| $N_2$ | | | | | | | | | | |
| $H_2SO_4$ | | | | | | | | | | |
| Total | 5191 | 5212 | 5328 | 9 | 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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 120 | 120 | 120 | 120 | 120 | 120 | amb. | 225 | 120 | amb. | amb. |
| **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 |

## 4.1.10 EQUIPMENT LIST

### ALUMINA FROM NITRIC ACID/CLAY PROCESS
### Clay Preparation Area

Truck Dump Hopper (4) - 70 ton receiving hopper of fabricated steel with vertical support legs. (1 spare)

Truck Dump Wobbler Feeder (4) - 350 ton/h, 60 in wide x 18 bar, 11-1/2 in pitch series with 2 in openings between bars. (1 spare)

Under Wobbler Feeder Belt Conveyor (4) - 350 ton/h. (1 spare)

Primary Crushers and Chutes (4) - 350 ton/h double roll crushers, feed size 12 in, product size - 2 in. (1 spare)

Primary Crusher Belt Conveyor (4) - 350 ton/h. (1 spare)

Stockpile Distributor Belt Conveyor (1) - 1,000 ton/h

Stockpile Enclosure (1) - 100,000 ton capacity, 200 ft x 600 ft, A-frame steel building

Stockpile Reclaim Hoppers (2) - 25 ton capacity. (1 spare)

Stockpile Wobbler Feeder (2) - 270 ton/h, 60 in wide 18 bar, 9 in pitch series with 3/4 in openings between bars. (1 spare)

Secondary Crusher Feed Belt Conveyor (2) - 300 ton/h

Secondary Crushers and Chutes (3) - 150 ton/h Hammermill, 2 in feed size, minus 3/4 in product size. (1 spare)

Secondary Crusher Discharge Belt Conveyor (2) - 300 ton/h

Secondary Crusher Bucket Elevator (2) - 250 ton/h

Secondary Crushing Screens and Chutes (3) - 150 ton/h, plus 3/4 in oversize, minus 20 mesh undersize. (1 spare)

Roll Compactor (4) - 35 ton/h, 10 in dia x 36 in, minus 20 mesh feed size, 3/4 in product size. (1 spare)

## EQUIPMENT LIST (Cont)

Roll Compactor Recirculation Belt Conveyor (1) - 100 ton/h

Raw Clay Surge Bin Feed Belt Conveyor (1) - 300 ton/h

Raw Clay Surge Bin (1) - 1,000 ton capacity, 24 ft dia x 73 ft str. side

Raw Clay Weighfeeders (2) - 150 ton/h

Calciner Feed Belt Conveyor (2) - 150 ton/h

Clay Calciner System (Fluid-Bed) (2) - three stage fluidized bed dryer with air heater - 19 ft dia calciner - primary cooler followed by secondary cooler for 135 ton/h feed and 95 ton/h product, gas scrubber included

Coal Pulverizers (4) - 2 units - 5 ton/h; 2 units - 2.5 ton/h at 20 mesh

Calcine Discharge Apron Feeder (2) - 95 ton/h

Calcine Bucket Elevator (2) - 190 ton/h. (1 spare)

Calcine Vibrating Screen (3) - 110 ton/h, 20 mesh screen. (1 spare)

Cage Mill Grinder (2) - 150 ton/h, 2-roll 60 in dia grinder, 20 mesh product size. (1 spare)

Cage Mill Discharge Belt Conveyor (2) - 200 ton/h

Storage Bin Bucket Elevator (2) - 200 ton/h. (1 spare)

Calcine Storage Bins (2) - 1,500 ton capacity, 30 ft dia x 88 ft str. side

Calcine Weighfeeders (4) - 200 ton/h. (2 spares)

Leach Tank Feed Conveyor (2) - 125 ton/h

EQUIPMENT LIST (Cont)

Chutes and Hoppers

Dust Collection System - baghouses with blowers, piping, and controls

Leaching, Thickening, Filtration Area

Calcined Clay Feeders (4) - 125 ton/h, totally sealed screw feeders. (2 spares)

Leach Tanks (8) - 16 ft dia x 35 ft str. side with draft tube constructed of carbon steel shell with polymeric membrane and acid-resistant brick lining. (2 trains)

Leach Tank Agitators (8) - mild agitation, 316 stainless steel construction

Leach Tank Condensers (8) - 1,000 $ft^2$ surface area, 304 stainless steel tubes, carbon steel shell

Leach Tank Recirculating Pumps (4) - 1,000 gal/min, 316 stainless steel construction. (2 spares)

Leaching Product Pumps (4) - 1,500 gal/min, 316 stainless steel construction. (2 spares)

Condenser Pumps (16) - 50 gal/min, 316 stainless steel construction. (8 spares)

Sand Thickener Tanks (5) - 106 ft dia x 15 ft str. side, carbon steel shell, covered and FRP-lined. Four units operating in parallel. (1 spare)

Sand Thickener Rakes (5) - 2-arm rakes, 304 stainless steel construction. (1 spare)

Underflow Pumps (10) - 350 gal/min, 316 stainless steel construction. (5 spares)

Overflow Pumps (10) - 650 gal/min, 316 stainless steel construction. (5 spares)

EQUIPMENT LIST (Cont)

Mud Washer Tanks (18) - 106 ft dia x 15 ft str. side, carbon steel shell, covered and FRP-lined. (2 trains - 9 unit CCD washing)

Mud Washer Rakes (18) - 2-arm rakes, 304 stainless steel construction

Mud Washer Underflow Pumps (36) - 750 gal/min, 316 stainless steel construction. (18 spares)

Mud Washer Overflow Pumps (36) - 675 gal/min, 316 stainless steel construction. (18 spares)

Washer Waste Tank (1) - 45,000 gal, 16 ft dia x 30 ft str. side, carbon steel with PVC lining

Washer Waste Pumps (2) - 2,500 gal/min, 316 stainless steel construction. (1 spare)

Flocculant Hoppers and Feeders (4) - 2 $ft^3$ capacity hoppers, 8 gal/min feeders, 304 stainless steel construction

Flocculant Mix Tank (1) - 3,000 gal, 8 ft dia x 8 ft str. side, 304 stainless steel construction

Flocculant Mix Tank Agitator (1) - mild agitation, 304 stainless steel construction

Flocculant Transfer Pump (2) - 100 gal/min, 316 stainless steel construction. (1 spare)

Flocculant Storage Tank (1) - 10,000 gal, 10 ft dia x 18 ft str. side, 304 stainless steel construction

Flocculant Solution Pump (2) - 6.25 gal/min, 316 stainless steel construction. (1 spare)

Sump Relay Tank (1) - 95,000 gal, 27 ft dia x 22 ft str. side, rubber-lined carbon steel construction

EQUIPMENT LIST (Cont)

Sump Relay Pumps (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Wash Water Relay Tank (1) - 150,000 gal, 30 ft dia x 30 ft str. side, rubber-lined carbon steel construction

Wash Water Relay Pump (2) - 1,500 gal/min, 316 stainless steel construction. (1 spare)

Filter Press and Repulpers (5) - 2,500 $ft^2$ filter area with retractable shells. 820 gal/min feed, 304 stainless steel construction. (2 spares)

Collecting Sluice (1) - common sluice of 304 stainless steel construction

Sluice Screen (2) - 4 ft 6 in x 5 ft 4 in 304 stainless steel construction. (1 spare)

Press Cake Tanks (2) - 4,600 gal, 10 ft dia x 8 ft str. side, butyl rubber-lined carbon steel shell

Repulped Slurry Pumps (4) - 200 gal/min, 316 stainless steel construction. (1 spare)

Filter Aid Storage Tank (1) - 100 ton capacity, 12 ft dia x 30 ft str. side, carbon steel construction

Filter Aid Conveyor and Weighfeeder (1) - 5 ton/d capacity

Filter Aid Slurry Tank (2) - 2,500 gal, 7 ft dia x 9 ft str. side, butyl rubber-lined carbon steel. (1 spare)

Filter Aid Slurry Tank Agitators (2) - 100% solid suspension, 316 stainless steel construction. (1 spare)

Filter Aid Slurry Pumps (2) - 25 gal/min, 316 stainless steel construction. (1 spare)

Filter Aid Liquor Pumps (2) - 20 gal/min, 316 stainless steel construction. (1 spare)

EQUIPMENT LIST (Cont)

Spent Filter Aid Dumpers (4) - portable bins

Filtrate Surge Tank (1) - 290,000 gal, 42 ft dia x 28 ft str. side, butyl-lined carbon steel

Filtrate Pumps (2) - 2,500 gal/min, 316 stainless steel construction. (1 spare)

Wash Water Storage Tank (1) - 500,000 gal, 45 ft dia x 42 ft str. side, rubber-lined carbon steel

Wash Water Storage Tank Pumps (3) - 2,500 gal/min, 316 stainless steel construction. (1 spare)

Solvent Extraction-HCl Stripping Area

Pregnant Liquor Surge Tank (1) - 600,000 gal, 36 ft dia x 70 ft str. side, butyl-lined carbon steel

Pregnant Liquor Surge Pumps (2) - 2,450 gal/min, 316 stainless steel construction. (1 spare)

Mixing-Settling Tanks (22) - 56 ft x 18 ft x 10 ft concrete tanks with FRP lining

Mixing-Settling Tank Covers (22) - segmented self-supporting FRP construction

Mixer-Settler Head Tanks (16) - 2,000 gal, FRP construction

Pumping-Mixing Turbines and Baffles (22) - 316 stainless steel turbines, FRP baffles

Mixer-Settler Overflow (22) - FRP construction

Kerosene Unloading Pump (2) - 200 gal/min, ductile iron construction. (1 spare)

Kerosene Storage Tank (1) - 7,000 gal, 10 ft dia x 12 ft str. side carbon steel construction.

EQUIPMENT LIST (Cont)

Kerosene Blend Pump (2) - 250 gal/min, ductile iron construction. (1 spare)

DEHPA Unloading Pump (2) - 200 gal/min, ductile iron construction. (1 spare)

DEHPA Storage Tank (1) - 10,000 gal, 10 ft dia x 18 ft str. side, carbon steel construction

DEHPA Blend Pump (2) - 250 gal/min, ductile iron construction. (1 spare)

DEHPA Heater (1) - carbon steel shell and tube heat exchanger

Solvent Blend Tank (1) - 4,000 gal, 8 ft dia x 11 ft str. side, carbon steel construction

Solvent Blend Tank Agitator (1) - thorough agitation, 304 stainless steel construction

Solvent Blend Tank Load Cell (1) - 25,000 lb load cell, 6-h cycle to fill, agitate, and empty

Solvent Surge Tank (1) - 30,000 gal, 16 ft dia x 18 ft str. side, carbon steel construction

Solvent Surge Transfer Pumps (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Unwashed Loaded Solvent Pumps (4) - 500 gal/min, 316 stainless steel construction. (2 spares)

Unwashed Loaded Solvent Tank (1) - 30,000 gal, 16 ft dia x 18 ft str. side, carbon steel construction

Unwashed Loaded Solvent Transfer Pumps (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Loaded Solvent Pumps (4) - 500 gal/min, 316 stainless steel construction. (1 spare)

## EQUIPMENT LIST (Cont)

Loaded Solvent Tank (1) - 30,000 gal, 16 ft dia x 18 ft str. side, carbon steel construction

Loaded Solvent Transfer Pump (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Spent HCl Pumps (4) - 350 gal/min, polypropylene-lined cast iron. (2 spares)

Unwashed Solvent Pumps (4) - 500 gal/min, polypropylene-lined cast iron. (2 spares)

Unwashed Solvent Storage Tank (1) - 30,000 gal, 16 ft dia x 18 ft str. side, carbon steel construction

Unwashed Solvent Transfer Pumps (2) - 1,000 gal/min, polypropylene-lined cast iron. (1 spare)

Solvent Pumps (4) - 500 gal/min, polypropylene-lined cast iron construction. (2 spares)

Solvent Blend Tank Pumps (2) - 50 gal/min, ductile iron construction. (1 spare)

Spent HCl Solution Static Mixer (1) - in-line fluoropolymer-lined mixer

HCl Recovery Evaporation Reboilers (4) - 3,000 $ft^2$ heat transfer area, impervious graphite tubes and heads, carbon steel shell

HCl Recovery Surge Tanks (2) - 6,000 gal, 10 ft dia x 10 ft str. side, glass-lined carbon steel shell

HCl Recovery Surge Tank Agitator (2) - PVC-lined

HCl Recovery Condenser (4) - 3,500 $ft^2$ heat transfer area, impervious graphite tubes and heads, carbon steel shell

HCl Recovery Slurry Pumps (3) - 75 gal/min, PVC-lined cast iron. (1 spare)

EQUIPMENT LIST (Cont)

Recovery HCl Transfer Pump (3) - 360 gal/min, PVC-lined cast iron. (1 spare)

HCl Storage Tank (1) - 130,000 gal, 30 ft dia x 24 ft str. side, rubber-lined carbon steel

HCl Transfer Pumps (2) - 60 gal/min, rubber-lined cast iron construction. (1 spare)

$H_2SO_4$ Storage Tank (1) - 100,000 gal, 24 ft dia x 30 ft str. side, carbon steel construction

$H_2SO_4$ Unloading Pump (2) - 500 gal/min, 316 stainless steel construction. (1 spare)

$H_2SO_4$ Transfer Pump (2) - 50 gal/min, 316 stainless steel construction. (1 spare)

Raffinate Pump (4) - 1,250 gal/min, 316 stainless steel construction. (2 spares)

Raffinate Surge Tank (1) - 300,000 gal, 35 ft dia x 42 ft str. side, butyl-lined carbon steel construction

Raffinate Transfer Pump (4) - 2,500 gal/min, 2 pumps in series to obtain 140 ft TDH, 316 stainless steel construction. (2 spares)

Solvent Extraction Sump (1) - 30,000 gal, 18 ft x 18 ft x 13 ft deep FRP-lined concrete

Solvent Extraction Sump Covers - segmented self-supporting FRP construction

Solvent Extraction Sump Skimmer (1) - Kerosene skimmer - FRP construction

Solvent Extraction Sump Pumps (2) - 2,900 gal/min, ductile iron construction. (1 spare)

Skimmed Solvent Pumps (2) - 50 gal/min, ductile iron construction. (1 spare)

# EQUIPMENT LIST (Cont)

## Heat Interchange, Evaporation, Crystallization, Centrifuging Area

Heat Interchange Flash Tanks (5) - 9 ft dia x 10 ft str. side. Feed filtrate @ 2,500 gal/min goes into standpipe with cone deflector baffle at pipe discharge. Discharge at cone bottom with vortex breaker. Demisters required at vapor outlet. Flash tank pressures: 1st stage - 9.5 psia, 5th stage - 3 psia. 304 stainless steel construction

Heat Interchange Heat Exchangers (4) - 7,500 $ft^2$ heat transfer area. 304 stainless steel

Heat Interchange Barometric Condenser (1) - with steam ejectors to develop 3 psia. 304 stainless steel construction

Heat Interchange Pumps (10) - 2,500 gal/min, 316 stainless steel construction. (5 spares)

Heat Interchange Hotwell (1) - 6,000 gal, 10 ft x 8 ft deep FRP-lined concrete

Heat Interchange Hotwell Covers - segmented self-supporting FRP construction

Heat Interchange Hotwell Pumps (2) - 100 gal/min, 316 stainless steel construction. (1 spare)

Pregnant Liquor Evaporators (3) - single effect system, complete with pumps, heating elements, preheaters, vapor pipe, surface condenser, and 2-stage ejector with barometric condenser. 304 stainless steel construction

Evaporator Hotwell (1) - 6,000 gal, 10 ft x 16 ft x 8 ft deep FRP-lined concrete

Evaporator Hotwell Cover - segmented self-supporting FRP construction

Evaporator Hotwell Pumps (2) - 100 gal/min, 316 stainless steel construction. (1 spare)

EQUIPMENT LIST (Cont)

Two Stage Crystallizers (10) - 24 ft dia x 18 ft str. side crystal suspension containers, 12 ft dia x 10 ft str. side vaporizers, central pipes, circulating piping, circulating pumps, vapor piping, and two-stage ejectors with barometric condensers. 304 stainless steel construction

Crystallizer Product Pumps (20) - 300 gal/min, 316 stainless steel construction. (10 spares)

Crystallizer Hotwell (1) - 6,000 gal, 10 ft x 10 ft x 8 ft deep FRP-lined concrete

Crystallizer Hotwell Cover - segmented self-supporting FRP construction

Crystallizer Hotwell Pumps (2) - 100 gal/min, 316 stainless steel construction. (1 spare)

Crystallizer Dump Tank (1) - 50,000 gal, 18 ft dia x 25 ft str. side. 304 stainless steel construction. (Normally empty)

Crystallizer Dump Tank Pumps (2) - 500 gal/min, 316 stainless steel construction. (Emergency use only)

Crystallizer Dump Tank Heat Exchanger (1) - 500 $ft^2$ heat transfer area. 304 stainless steel tubes, carbon steel shell

Centrifuge Feed Slurry Tanks (2) - 100,000 gal, 30 ft dia x 20 ft str. side, butyl rubber-lined carbon steel construction

Centrifuge Feed Pumps (9) - 450 gal/min, 316 stainless steel construction. (1 spare)

Mother Liquor Recycle Tanks (2) - 40,000 gal, 18.5 ft dia x 20 ft str. side, butyl rubber-lined carbon steel

Centrifugation Purge Pumps (3) - 250 gal/min, 316 stainless steel construction. (1 spare)

Evaporator Recycle Feed Pumps (3) - 650 gal/min, 316 stainless steel construction. (1 spare)

EQUIPMENT LIST (Cont)

Cyclone Receiver Tanks (2) - 2,000 gal, FRP construction

Cyclone Classifiers (9) - 18 in dia cyclones, feedrate of 430 gal/min, underflow at 65% solids based on 1.7 Sp. Gr. differential. FRP housing with butyl rubber lining. (1 spare)

Centrifuges (9) - pusher type, 60 ton/h discharge solids, basket drive - 100 hp, push plate drive - 60 hp. 304 stainless steel construction. (1 spare)

Centrate Collection Tanks (2) - 15,000 gal, 16 ft dia x 10 ft str. side. Butyl rubber-lined carbon steel

Centrate Pumps (3) - 300 gal/min, 316 stainless steel construction. (1 spare)

Centrifuge Discharge Screw Conveyors (9) - 2,000 $ft^3/h$ or 70 ton/h, 10 ft long, sealed. 304 stainless steel construction. (1 spare)

Wet Crystal Surge Bin Bucket Elevator (3) - 8,000 $ft^3/h$ or 280 ton/h, 304 stainless steel construction. (1 spare)

Purge Nitrate Storage Tanks (2) - 12,000 gal, 12 ft dia x 15 ft str. side. Butyl rubber-lined carbon steel

Product Melting, Decomposition, Calcination Area

Wet Crystal Surge Tanks (2) - 250 ton capacity, 16 ft dia x 32 ft str. side, butyl rubber-lined carbon steel

Wet Crystal Surge Tank Conveyors (4) - 250 ton/h, 304 stainless steel construction. (2 spares)

Melt Tank Bucket Elevators (3) - 250 ton/h, 304 stainless steel construction. (1 spare)

Product Melt Tanks (3) - 50,000 gal, 16 ft dia x 32 ft str. side with draft tube. 304 stainless steel construction. (1 spare)

EQUIPMENT LIST (Cont)

Product Melt Tank Agitators (3) - 72 in propeller with six blades. 316 stainless steel construction

Product Melt Tank Steam Coils (3) - 1 in dia steam coil for 41.7 x $10^6$ Btu/h heat transfer. 316 stainless steel construction

Product Melt Tanks Pumps (6) - 800 gal/min, 316 stainless steel construction. (3 spares)

Product Decomposers (19) - 20 ft dia x 25 ft str. side with spray headers, recirculation gas header, and stainless steel diaphragm. Constructed of carbon steel shell with PVC membrane, castable refractory and brick lining. Included are product cyclones (19) - 12 ft dia x 20 ft str. side. Constructed of carbon steel shell with PVC membrane, castable refractory and brick lining

Product Heat Exchangers (19) - 1 in dia tubes with fins for 54.5 x $10^6$ Btu/h heat transfer service. 316 stainless steel construction

Dowtherm "A" Heat Transfer System (5) - 200 x $10^6$ Btu/h system, including coal pulverizer, coal and limestone feed hoppers, feed system, combustion air blower, fluidized bed combustor with start-up system, Dowtherm coils, cyclone collector, air preheater, circulating pumps, flash tanks, expansion tanks, and temperature controls

Recycle Gas Blowers (19) - inlet conditions: 21.4 ton/h of 7% $HNO_3$, air 27% $H_2O$, 66% air temp = 180°F., pressure = 14.7 psia. Discharge conditions: temperature = 190°F., pressure = 21.7 psia. Constructed of 304 stainless steel

Heat Transfer System Coal Pulverizers (5) - 11.5 ton/h at 20 mesh

Heat Transfer System Ash Handling (5) - 1.1 ton/h system with blowers, piping, cyclone, and ash bin

EQUIPMENT LIST (Cont)

Heat Transfer System $SO_2$ Scrubbers (5) - 76,200 SCFM, vertical wet approach. Venturi scrubber, flooded elbow and cyclone separator capable of removing 99% of fly ash and dust and 96% of $SO_2$

Product Decomposer Discharge Screw Conveyor (19) - 3.5 ton/h, 304 stainless steel construction

Surge Bin Feed Conveyor (2) - 35 ton/h, 304 stainless steel construction

Waste Heat Boilers (5) - capacity of 85,000 lb/h of 100 psig steam supplied with 350,000 lb/h of 1300°F waste gas

Calciner Feed Surge Bin Bucket Elevator (2) - 65 ton/h, 304 stainless steel construction with heat resistant bearings. (1 spare)

Calciner Feed Surge Bin (1) - 1,000 ton capacity, 30 ft dia x 50 ft str. side 304 stainless steel construction

Surge Bin Recirc. Screw Conveyor (1) - 65 ton/h, 304 stainless steel construction

Product Calciner System (1) - capacity = 65 ton/h. Consisting of 6 ft dia x 25 ft str. side suspension preheater cyclone, 7-1/2 ft dia x 35 ft product recovery cyclone, 13-1/2 ft dia x 25 ft fluidized bed calciner, 6 ft x 17 ft x 10 ft primary cooler - air preheater, 4 ft x 40 ft x 8 ft secondary cooler, no. 6 fuel oil burner system. Feed temperature = 750°F, product temperature = 180°F. Horsepower requirement is 750 hp. Carbon steel construction with castable refractory and brick lining

Alumina Conveying System (2) - 40 ton/h pneumatic conveying system with blower package, 8 in conveying line, surge hopper, binvents and fan

Alumina Silos (2) - 7,500 ton capacity, 50 ft dia x 50 ft str. side with 60° cone bottom. Carbon steel construction

EQUIPMENT LIST (Cont)

Bleed Stream Evaporation, Melting, Decomposition Area

Bleed Stream Evaporator (3) - single effect system complete with circulating pumps, heating elements, preheaters, vapor piping, surface condenser, and 2-stage ejector with barometric condenser. Constructed of 304 stainless steel

Bleed Stream Evaporator Product Pumps (2) - 400 gal/min, 316 stainless steel construction. (1 spare)

Bleed Stream Evaporator Hotwell (1) - 6,000 gal, 10 ft x 10 ft x 8 ft deep concrete with FRP lining

Bleed Stream Evaporator Hotwell Pumps (2) - 100 gal/min, 316 stainless steel construction. (1 spare)

Bleed Stream Evaporator Hotwell Cover - segmented self-supporting FRP construction

Bleed Stream Melt Tanks (2) - 25,000 gal, 13 ft dia x 25 ft str. side, 304 stainless steel construction

Bleed Stream Melt Tank Agitators (2) - 100% solid suspension, 316 stainless steel construction

Bleed Stream Melt Tank Heat Coils (2) - 1 in diameter coils for $4.3 \times 10^6$ Btu/h heat transfer capacity. 316 stainless steel construction

Bleed Stream Melt Tank Pumps (4) - 400 gal/min, 316 stainless steel construction. (2 spares)

Bleed Stream Decomposer System (2) - 20 ft dia x 25 ft str. side with spray headers, recirculation gas headers, stainless steel distributor and cyclone. Decomposer and cyclones are constructed of carbon steel shell with PVC membrane, castable refractory and brick lining. Included with the decomposer is a heat exchanger made of 1 inch 316 stainless steel tubes with fins for a heat transfer service of $40 \times 10^6$ Btu/h

## EQUIPMENT LIST (Cont)

Waste Slurry Tanks (2) - 10,000 gal, 12 ft dia x 8 ft str. side, carbon steel construction

Waste Slurry Pumps (4) - 500 gal/min, ductile iron construction

Waste Slurry Tank Agitators (2) - mild agitation, 316 stainless steel construction

Bleed Stream Recycle Blowers (2) - inlet conditions: 20 ton/h of 7% $HNO_3$, 27% $H_2O$, 66% air temp = 180°F, pressure = 14.7 psia. Discharge conditions: temperature = 190°F, pressure = 21.7 psia. Constructed of 304 stainless steel

Bleed Stream Venturi Scrubber (5) - gas rate of 30,000 ACFM at 750°F composed of 35% $H_2O$, 32% $HNO_3$ and 33% air. Scrubbing liquid is 57% $HNO_3$ at 1,590 gal/min with a pressure drop of 10 inches. 316 stainless steel construction with sump

Bleed Stream Cyclone Separator (5) - 6.5 ft dia x 13 ft str. side with tangential inlet from venturi scrubber. Outlet gas of 19 ton/h is composed of 7% $HNO_3$, 27% $H_2O$ and 66% air. Discharge liquid is 1,650 gal/min at 170°F of 57% $HNO_3$

Bleed Stream Recirculation Pumps (10) - 1,650 gal/min, 316 stainless steel construction. (5 spares)

Bleed Stream Liquor Coolers (5) - 7,400 $ft^2$ heat transfer surface, 304 stainless steel tubes, carbon steel shell

Coal Pulverizers (1) - 6 ton/h at 20 mesh

Bleed Stream Heat Transfer System (1) - 100 x $10^6$ Btu/h system, including coal pulverizer, feed hoppers, feed system, combustion air blower, and fluidized bed combustor with start-up system. Dowtherm coils, cyclone collector, air preheater, circulating pumps, flash tanks, expansion tanks, and temperature controls

Waste Heat Recovery Boiler (1) - capacity of 45,000 lb/h of 100 psig steam supplied with 200,000 lb/h, 1,300°F waste gas

## EQUIPMENT LIST (Cont)

### $NO_x$ Removal and Acid Recovery Area

Acid Recovery Venturi Scrubbers (19) - gas rate of 30,000 ACFM at 750°F composed of 35% $H_2O$, 32% $HNO_3$, and 33% air. Scrubbing liquid is 57% $HNO_3$ at 1,590 gal/min with a pressure drop at 10 inches. 316 stainless steel construction with sump

Acid Recovery Cyclone Separators (19) - 6.5 ft dia x 13 ft str. side with tangential inlet from venturi scrubber. Outlet gas of 19 ton/h is composed of 7% $HNO_3$, 27% $H_2O$ and 66% air. Discharge liquid is 1,650 gal/min at 170°F of 57% $HNO_3$

Acid Recovery Circulating Pumps (38) - 1,650 gal/min, 316 stainless steel construction. (19 spares)

Acid Recovery Circulating Coolers (19) - 7,400 $ft^2$ heat transfer surface, 316 stainless steel tubes, carbon steel shell

Catalytic Combustion System (1) - break up $NO_x$ to $N_2$ from gases composed of 6 ton/h of $NO_x$, 13.5 ton/h of $H_2O$ and 30.5 ton/h of air. Heat requirement = 104 x $10^6$ Btu/h. Quench system included to avoid reformation of $NO_x$

$HNO_3$ Storage Tanks (3) - 42,000 gal, 20 ft dia x 18 ft str. side, 304 stainless steel construction

$HNO_3$ Recovery Product Pumps (2) - 1,400 gal/min, 316 stainless steel construction

50% $HNO_3$ Leach Feed Pumps (3) - 1,500 gal/min, 316 stainless steel construction

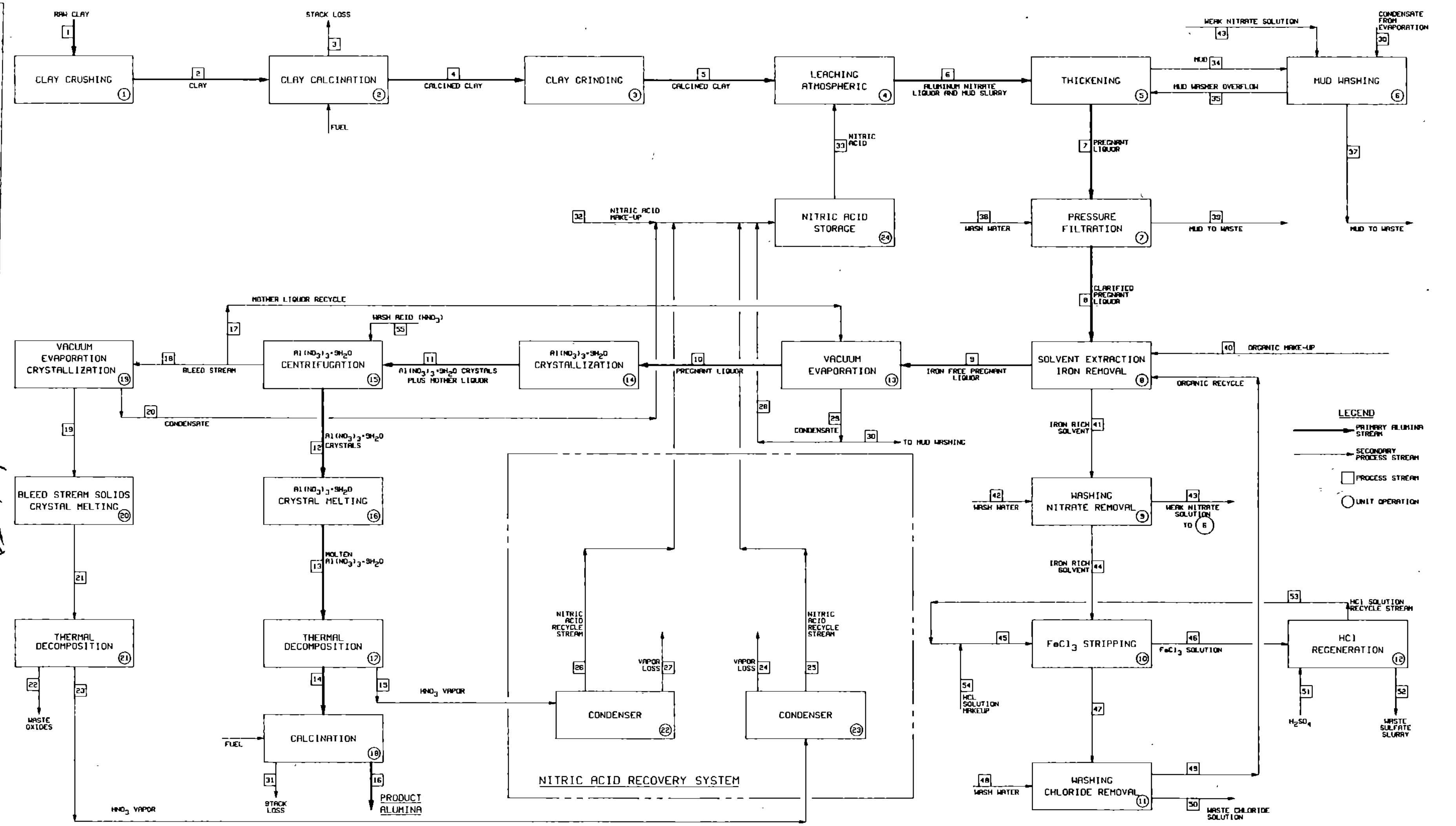
### Utilities

Steam Plant and Auxiliary Systems (1) - 150,000 lb/h coal-fired boiler, 125 psig saturated steam. Complete with controls, ash handling, fly ash and $SO_2$ scrubber, feed water and condensate system, and coal pulverizers

## EQUIPMENT LIST (Cont)

Cooling Towers and Auxiliary Systems (1) - 31,000 gal/min from 130°F to 90°F at 80°F ambient wet bulb. Horsepower requirement is 600. Pumps and basin are included

4-1-50

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NOTES

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

FOR INFORMATION ON HEAT, STEAM & COOLING WATER REQUIREMENTS SEE TABLE 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

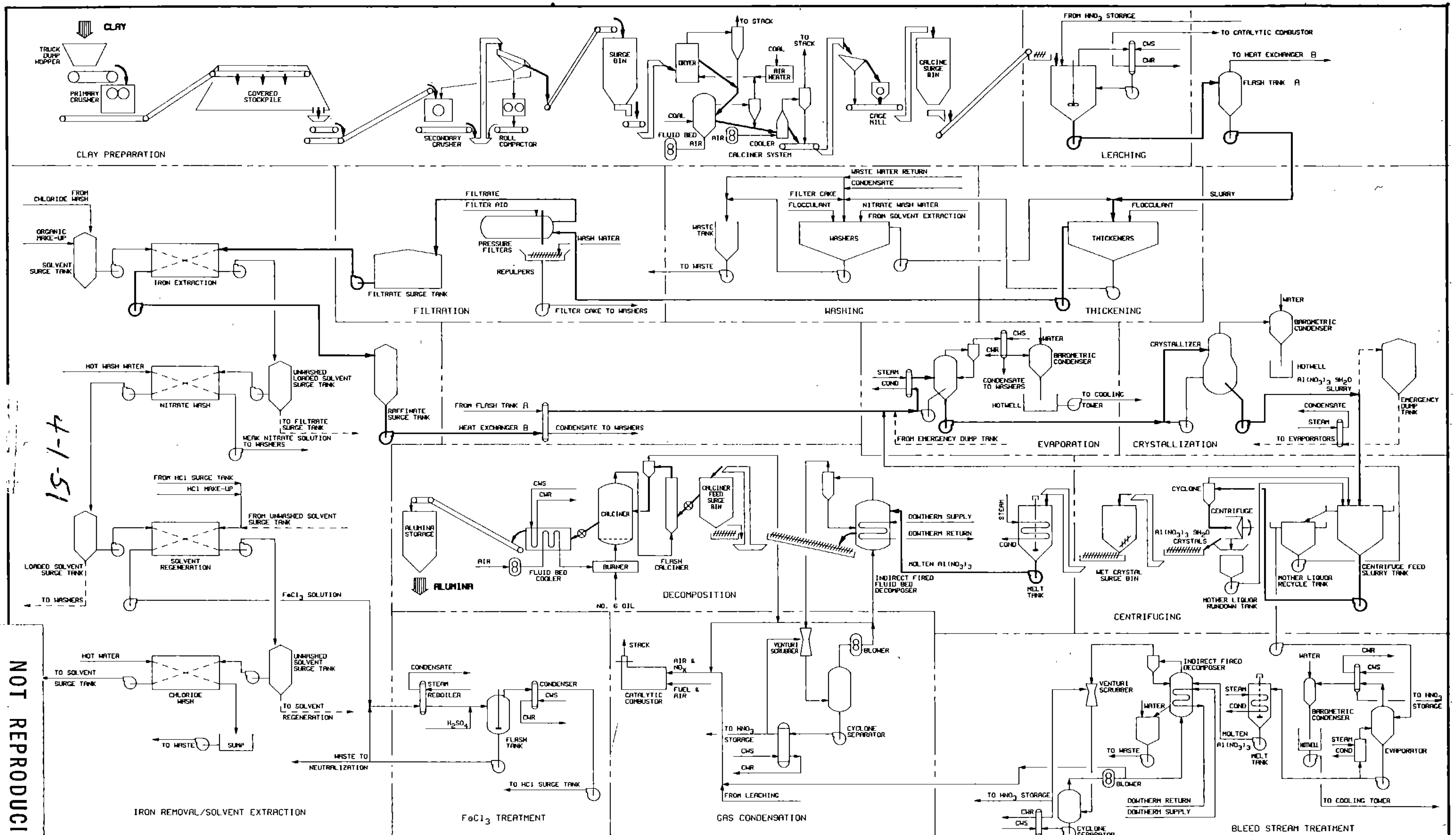
PROFESSIONAL SEAL

**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
NITRIC ACID PROCESS

JOB No. 76161-002 | DWG. No. FIGURE NO. 4-1-2 | REVISION R-1




CWR - COOLING WATER RETURN
CWS - COOLING WATER SUPPLY
EQUIPMENT AS DEPICTED IN THIS DIAGRAM IS CONCEPTUAL AND IS PRESENTED FOR GRAPHICAL PURPOSES ONLY AND DOES NOT NECESSARILY REFLECT ACTUAL EQUIPMENT THAT MAY BE USED FOR THE PROCESS EITHER IN QUANTITY OR IN CONCEPT.
HEAVY LINE INDICATES MAIN STREAM.

| NO. | DATE | REVISION | BY | CHK | APP | APP. | NOTES |
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DESCRIPTION | COST ACCOUNT
WORK COVERED BY THIS DRAWING CHARGED TO COST ACCOUNT ABOVE

CONSTRUCTION APPROVAL | APPROVAL | DATE | SCALE: NONE | DATE | PROFESSIONAL SEAL

DESIGNED BY / DRAWN BY / CHECKED BY / APPROVED BY / APPROVED BY

**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
NITRIC ACID
PROCESS CONCEPT

JOB No. 76161-002 | DWG. No. FIG NO. 4-1-3 | REVISION R-1

4-1-51

NOT REPRODUCIBLE

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

### 4.2.1 Summary and Conclusions

The extraction of alumina from clay via hydrochloric acid extraction followed by HCl-induced crystallization of pure $AlCl_3 \cdot 6H_2O$ and then thermal decomposition of this salt is actually a composite of several older processes designed specifically for high quality U.S. clays containing high ratios of acid-soluble alumina to impurities. The process seeks to minimize the work done on the primary reagent (alumina-bearing) stream as a means of reducing the cost of recovering the pure alumina to a minimum.

This process, illustrated by the flowsheet shown in Figure 4-2-1, includes the following steps:

(1) Calcination of clay.

(2) Leaching of the calcine at atmospheric pressure and at the boiling temperature 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, rejecting iron as a dilute $FeCl_3$ solution.

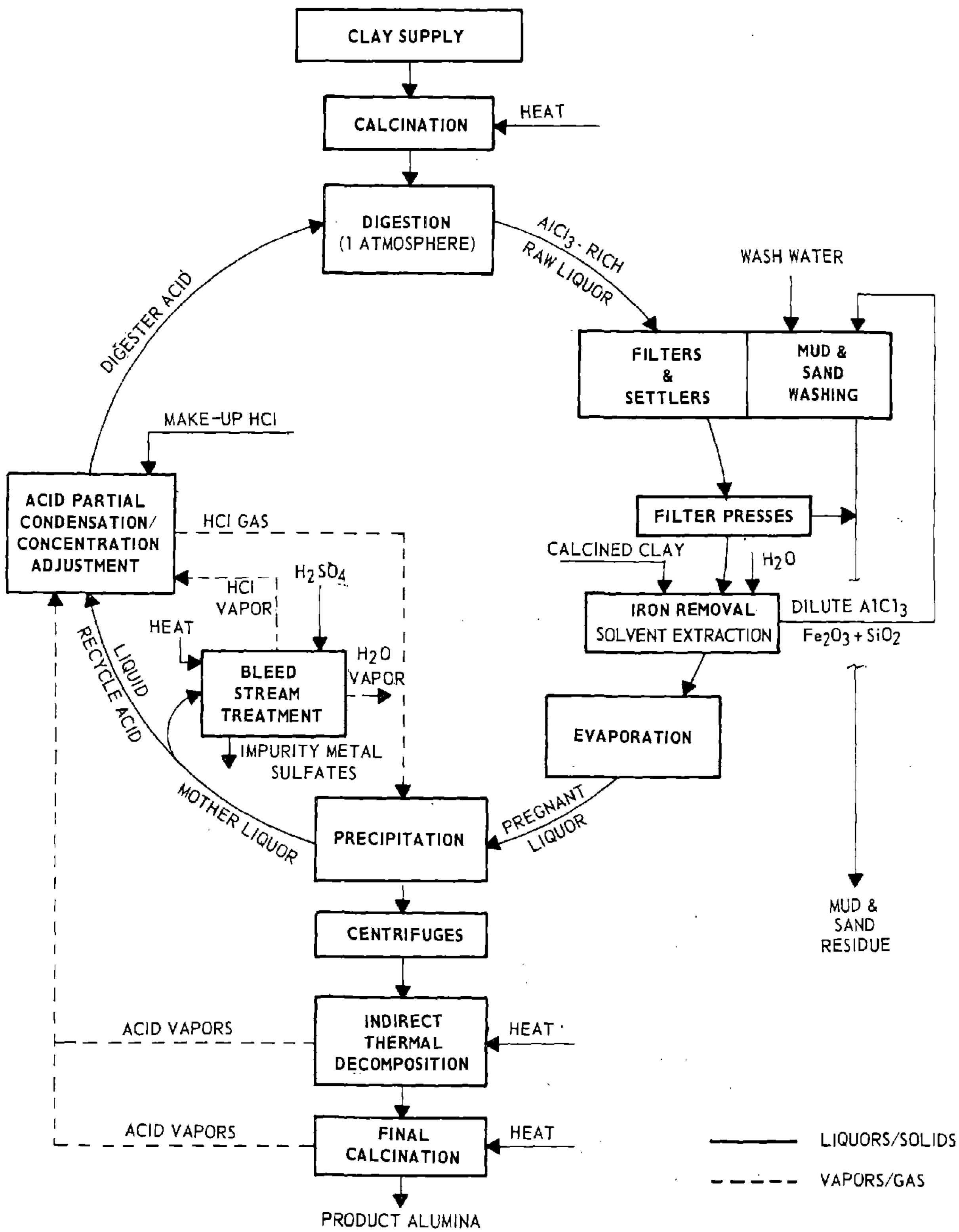
(5) Concentration by evaporation of the solution from which the iron has been removed.

(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 4-2-1

## ALUMINA FROM CLAY VIA HCl GAS-INDUCED CRYSTALLIZATION



(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) Reaction of the iron extract obtained in (4) with a moderate excess of alumina in the form of calcined clay to produce a dilute solution of $AlCl_3$ containing a suspension of $Fe_2O_3$ deposited upon the residual portion of the added calcine. This slurry may be returned to the solid-liquid separation step (3) at an appropriate point for recovery of the dissolved $AlCl_3$ and rejection of the waste solids to tailings.

(12) Recovery of heat from steps (9) and (10), or from any other source, for use in the remainder of the process as appropriate.

The process 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 by this process. The estimated thermal energy requirement as fuel to process, with reasonable engineering for heat recovery, is $20.9 \times 10^6$ Btu/ton product alumina.

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 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 the indirectly fired thermal decomposition of $AlCl_3 \cdot 6H_2O$ may be furnished by any economical fuel, including coal. Preliminary studies show it is probable that energy required for the calcination of clay may 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.

Two major technological problems require solution before design of a demonstration plant can be undertaken with a reasonable probability of economically successful operation. The first, and probably more difficult of these, 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.

The second major technical problem requiring solution is that of optimizing the tradeoffs between allowable concentrations of impurities which may be present in the crystallizer mother liquor, bleed stream processing costs, the percent recovery of dissolved $AlCl_3$ per pass through crystallization, the attainable production of $AlCl_3 \cdot 6H_2O$ crystals per unit time per unit crystallizer volume, and the effort spent on washing mother liquor from the crystals produced, all while making crystals decomposable to alumina meeting reduction quality specifications.

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.

Clay calcination, leaching, and solid-liquid separation are interdependent. Operable process sections could be designed today on the basis of existing information to carry out these functions, but further study of these steps holds great promise for energy, other operating costs, and capital savings.

No process for the extraction of alumina from clay could be operated that does not almost completely preclude the escape of HCl either as vapor or as liquid to the environment. Fortunately, HCl is chemically very stable, and the nature of the system $HCl-H_2O$ is such that the concentration of HCl in vapor in equilibrium with concentrations of HCl in $H_2O$ below about eight weight percent HCl is practically zero. This makes possible virtually complete recovery of HCl from gases which must be vented. Impurity metals, with the exception of iron, are discharged from the process as sulfates; and provision is made for return to the process of some chloride unavoidably sent to tailings with the acid-insoluble part of the entering clay. Makeup HCl requirements are thereby kept low and environmental problems minimized.

### 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 two 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 150 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) With increasing temperature, the solubility of chlorides tends to increase to varying degrees. Scaling problems on heat transfer surfaces are therefore eliminated or greatly reduced.

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 known--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.

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. Nonvolatile 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 recently developed solvent extraction technology mentioned above 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.

The hydrochloric acid extraction-hydrogen chloride precipitation process is built upon the efforts of the early investigators. It draws upon newer technology and more recently available data in an attempt to solve previous extremely difficult problems, all with the goal of producing alumina at the lowest possible cost.

## 4.2.3 The Process

### 4.2.3.1 Summary

This process employs 25-27% hydrochloric acid for leaching and therefore directly produces a leach liquor requiring a minimum of evaporation. Iron is removed by solvent extraction which rejects it in the form of a dilute $FeCl_3$ extract. The latter is treated with calcined clay, precipitating $Fe_2O_3$ and forming a dilute $AlCl_3$ solution. The solids are discarded and the $AlCl_3$ solution is returned to the primary liquor stream. Following evaporation, the 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 final 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 the 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 first subjected to further crystallization at a higher hydrogen chloride concentration for the recovery of dissolved aluminum chloride. Subsequently, it is mixed with a large amount of hot concentrated waste chlorides in a column provided with a reboiler as a heat source at its base. HCl is desorbed and leaves at the top of the column, the water content of the bleed stream remaining almost entirely with the waste chlorides. The latter solution is separately reconcentrated and recycled. The water vapor is rejected and the net production of waste chlorides is withdrawn for recovery of chloride values by treatment with $H_2SO_4$.

### 4.2.3.2 Clay Calcination

The calcination of clay, including the probable utility of fluidized solids techniques in reducing the cost of calcination, was discussed in the section on alumina extraction via nitric acid. All comments made there on calcination and on the interrelationship between calcination, leaching, and solid-liquid separation apply equally to the extraction of alumina from clay via hydrochloric acid.

### 4.2.3.3 Leaching

Alumina dissolves during leaching as follows:

$$Al_2O_3 \cdot 2SiO_2 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O + 2SiO_2$$

$$\Delta H = 1446 \text{ Btu/lb } Al_2O_3$$

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 be sealed 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 concurrently in three to five stages at one atmosphere and at the boiling temperature with extraction of 90-98% of the total entering aluminum within a total residence time of about two hours.

Adequate information is available today for the design of a successful leaching operation. 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 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.

4.2.3.5 Iron Removal

The removal of iron is desirable to insure that it does not enter crystallization, thereby assuring 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:

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

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:

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

The strip solution produced during regeneration of the organic extractant is acidic and contains approximately 3.5% ferric chloride. Enough information has been developed about this operation to permit design of a demonstration plant without further development work. The $FeCl_3$ strip solution is heated to boiling and then slurried with calcined clay containing alumina in approximately 50% excess for the reaction.

$$Al_2O_3 \cdot 2SiO_2 + 2FeCl_3 \rightarrow Fe_2O_3 + SiO_2 + 2AlCl_3$$

calcine solution waste solids solution

The $Fe_2O_3$ tends to precipitate on the surface of and within the pores of the insoluble portion of the calcine clay particles, producing a readily filterable waste solid. Experimentally, it was found that 99.5% or more of the iron can be removed from the iron extract by adding an amount of calcined clay containing a 50% excess of contained alumina in relation to iron and by holding the slurry at boiling for two hours. An equivalent amount of aluminum goes into solution replacing the iron as indicated in the above equation.

The solids may be separated from this dilute $AlCl_3$ solution and a second amine hydrochloride extraction performed if the recovery of a compound such as $GaCl_3$ or the control of any metallic element forming an anionic chloride complex is desired. Following the second extraction, the raffinate dilute $AlCl_3$ solution may be added in partial substitution for wash water at an appropriate point in the solid-liquid separation. If no second extraction is performed, the dilute $AlCl_3$ slurry may be added to the waste residue washing system, rejecting $Fe_2O_3$, $SiO_2$, and unreacted clay to tailings along with acid insolubles from the primary leaching step. Very little or no $Fe_2O_3$ is expected to redissolve at this point, because nearly all of the acid originally added to leaching was consumed during that step, and because of the dilution. Any soluble iron forming or present will, of course, be removed in the subsequent solvent extraction of the primary liquor stream.

This method of iron separation-extract treatment rejects the iron from the overall process as oxide without consumption of reagent and at only a very small expenditure of energy. Acid used to leach iron is returned to the process in the form of $AlCl_3$. A small amount of $AlCl_3$ either coextracted with $FeCl_3$ or mechanically carried over into the extract, along with organic either dissolved in or mechanically entrained in the extract, is also returned to the process.

It is expected that the above-described overall approach to iron rejection will reduce the cost of rejecting iron from clay raw materials containing any reasonable amount of iron to a low percentage of the total cost of producing alumina from the clay.

#### 4.2.3.6 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.

Vapors produced during concentration will inevitably contain HCl. An advantageous manner of condensing these vapors would be in a direct contact vacuum condenser in which the recirculating warmed condensate would dissipate the heat of condensation to the environment evaporatively in a cooling tower. It is, however, absolutely necessary that no HCl be discharged to the environment through the cooling tower. A partial condenser has therefore been provided through which vapors exiting the evaporator will pass prior to entering the direct contact total condenser. The vapor-liquid equilibrium relationship in the system $HCl-H_2O$ is such that acid up to a concentration of 20% may be partially condensed (the maximum possible acid concentration depending upon the weight percent HCl in the vapor, assuming it to be less than 20%) while passing through uncondensed the excess of essentially pure $H_2O$ vapor. The latter passes to the direct contact total condenser. A method of providing further assurance that no HCl will escape is to add fresh water equivalent to that to be used in washing the waste solids to the circulating water, and then withdrawing water actually to be used for washing from the circulating water. This will keep the HCl concentration in the circulating water very low. A further minor advantage of this technique will be that warm wash water will be supplied to the waste residue washing system.

### 4.2.3.7 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

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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.

4.2.3.8 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 pressure 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 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.

The design of the crystal recovery and crystal washing section of a demonstration plant is straightforward, although it may turn out that meeting product specifications on some impurities with very low tolerance levels, such as $P_2O_5$, may depend to a major extent upon adequate washing. It may therefore be necessary to redesign the acid condensation system to provide more wash acid or to otherwise redesign crystal recovery to provide more efficient washing. Test work is required to answer these questions.

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.

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 375°F. The approximate reaction is

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

$$\Delta H = 4218 \text{ Btu/lb } Al_2O_3$$

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 14.4 x $10^6$ Btu/ton product alumina. No provision is included in the above requirement for steam that may be supplied in the final stage(s) of decomposition.

It is very desirable 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 comprised primarily of 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.

4.2.3.10 <u>Acid Recovery</u>

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 countercurrent 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 evaporation and 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) Storing or Removal from Storage of HCl Gas

There will be relatively short periods of time during which the crystallization section may be operating at reduced capacity or not at all when the decomposer is operating and producing HCl at some rate. There will be other times, as for example startups, when the crystallizer will require HCl gas but the decomposer will be producing it at a reduced rate or not at all.

HCl gas may be placed into storage by feeding acid of greater than 20% but less than about 37% concentration to the absorber/condenser as required and lowering operating temperatures in this equipment by rejecting more heat. This will permit any excess of HCl generated in decomposition to be withdrawn and stored as concentrated liquid acid. It is further expected that during normal steady-state operation, matching the crystallizer HCl gas requirement to the production will be accomplished in the same manner.

The provision of HCl gas to the crystallizer in the absence of condensible vapors from decomposition requires an external source of heat to desorb HCl from concentrated acid in storage, which may be provided by a reboiler supplying vapors to the bottom of either or both of the absorber/condensers described above. Concentrated acid from storage is fed to the top of the units and the HCl stripped by rising vapors from the reboiler. Acid of not less than 20% HCl is returned to storage from the bottom of the units.

4.2.3.11 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 a bleed stream of about 8% of the final crystallizer mother liquor (filtrate) will be required for the design clay quality.

The first treatment of the bleed 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 centrifuged, recovered, and redissolved in the iron-free leach liquor proceeding to evaporation.

Further treatment of the centrate has three functions:

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

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

(3) rejection of water from the process.

The centrate is 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 60% $H_2O$ and 40% 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 centrate 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 45% 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 partial acid condenser for recovery of contained HCl and then to condensation.

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 from $H_2O$, and at least two vendors offer the required technology on a commercial scale. Other commercial installations have been reported in Eastern Europe, and a partially analogous operation has been reported in Israel. There appears 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 using indirect firing. 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.

### 4.2.4 Energy Requirements

The total energy which must be supplied to the process in the form of fuel is $20.9 \times 10^6$ Btu/ton of alumina. Details are shown in table 2-1. Approximately 90% of this amount can be supplied as coal, the remaining 10% will probably be supplied as oil.

Coal is used to fire the fluid-bed clay calciners, and coal-fired Dowtherm boilers are used to supply heat for aluminum chloride decomposition. Fuel oil is used directly to calcine alumina to prevent product contamination with ash.

A significant amount of process heat, equivalent to 5.7 x 10 Btu/ton $Al_2O_3$, is required for evaporation of the primary process stream. It is anticipated that all of this heat can be recovered as waste heat from the condensation and decomposition sections of the process. Part of this heat is available as steam generated in a waste heat boiler fired by the hot gases from the decomposer indirect-heating system stacks, and the balance of the heat is available from condensation of $HCl/H_2O$ vapor evolved in aluminum chloride decomposition.

The use of coal to calcine clay will require developmental testing.

### 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. 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.

Washed waste solids from leaching and iron extract conversion will comprise silica, a small amount of unreacted clay, iron oxide, 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. Current technology makes possible return to the process of chloride values accompanying the waste solids by decanting and draining water from the sealed off waste solids disposal areas. Return of this water to the process is possible because much of the heat entering the process is finally rejected to the environment in the form of water vapor, resulting in a substantial net evaporation.

Other waste solids from the process are mixtures of metal sulfates with alumina. 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 when high quality clay is the alumina source.

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.

### 4.2.6 Alumina Product Quality

Experimental evidence based upon literature reports, some direct laboratory work and some miniplant results, indicate the chemical purity of alumina produced from this process with respect to metals has the potential of being significantly 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. It is possible, in view of the extremely low $P_2O_5$ specification in the product alumina, that the problem of meeting this specification is largely that of adequately washing adhering mother liquor away from the $AlCl_3 \cdot 6H_2O$ crystals before decomposition. Further study of this matter is required.

Tests on small quantities of chloride process alumina have shown that it can be produced to meet current 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 specifications can also be met.

### 4.2.7 Materials of Construction

In any HCl system a major concern is the corrosion resistance of containment materials. This is further complicated in systems wherein combinations of HCl - $H_2O$, metal chlorides, particulates, and other contaminants are present. Additions of organic solvents complicate the corrosive environment and further limit materials selection. Continuing research, development, and investigative work with metals, ceramics, cements, conversion coatings, direct coatings, polymers, and FRP materials in HCl environments should be actively pursued.

Significant development programs will be required to define optimum materials and material combinations necessary for satisfactory service in these aggressive atmospheres. The effect of varying combinations of metallic chlorides and other contaminants in combination with the HCl media at a wide range of flow rates, entrained particulates, pressures, and temperatures is generally known but will still require specific evaluation of actual expected operating situations and conditions.

In the low temperature portions of the system more conventional materials may be used. Typically, these include:

- Linings/coatings on steel
  - Rubber
  - Acid brick
  - Polymers - Kynar, Teflon, Saran, Polypropylene, etc.
- Titanium and titanium alloys
- Zirconium and zirconium alloys
- Fibre reinforced plastics (FRP)
- Karbate - graphitic compounds
- Ceramics - glass materials

The use and applicability of the above materials would be dependent upon such conditions as analyses, temperature, and particulate content of process media. Generally, coated materials could be used for pipe, tanks, and pressure vessels whereas the solid materials would have application in items such as pump impellers, valve internals, and heat exchange tubing. The basis of selection would include the utilization of those materials having an adequate service life along with minimizing the contribution of harmful corrosion products to the product stream.

In those cases where coatings will be used in extremely aggressive HCl media, assurance of high coating quality and integrity is mandatory. Also, the substrate upon which the coating is attached must provide adequate resistance to the working fluid so that significant failure will not occur should the coating be penetrated.

4.2.7.1 Investigative Work

Investigative work covering the case of bare metals exposed to pregnant and mother liquors indicates that a welded Zirconium 702 alloy does not look promising at temperatures in excess of 150°F. In this case the problem has been that of significant corrosion attack on weld regions during tests at 185°F. It should be noted, however, that unwelded Zirconium apparently performed adequately at the 185°F temperature. It would therefore be expected that solid unwelded Zr 702 components, properly heat-treated, could have an adequate service life. A similar condition is that of the welded Zirconium alloy for all metals under consideration and would emphasize the need for comprehensive tests of welded specimens for all candidate metals.

Before firm selections and application recommendations can be made, dynamic testing programs utilizing process flow rates and typical particulate concentrations should be implemented, since some metals are dependent upon film formation for retardation of corrosion.

4.2.7.2 Candidate Materials

As of this report date the more promising candidate materials for the lower temperature service would be:

$< 180^{\circ}F$ -- Rubber-lined steel
$180^{\circ} - 350^{\circ}F$. Kynar/Teflon over steel or higher alloy metals
$> 350^{\circ}F$ -- Polymer and acid brick-lined components

In the higher temperature systems, above $350^{\circ}F$, bare metal serviceability is questionable. It would be expected that high alloy or pure metals such as Zr or Ta might perform adequately at these temperatures. However, uncertainties such as selective corrosion in weld areas and maintenance of protective films in abrasive flowing solutions need further investigation. Ceramic, conversion, and diffusion coatings on carbon steel and high alloys should be examined. Substantial, high integrity coatings could provide reasonable service life in these environments. Generally, in systems such as the decomposition stages, acid and refractory bricks appear to be satisfactory for vessel linings. Inconel and Hastelloy alloys are being examined at the Bureau of Mines College Park facility for adequacy and are being considered as hanger and container materials for refractory linings. Again, it is necessary to have a substrate material that has reasonable creep strength at elevated temperatures along with resistance to the HCl environment sufficient to avoid catastrophic corrosion failure should the working media penetrate the linings.

4.2.7.3 Process Area and Materials Review

Following is a general review of several process areas and the materials considered for fabrication of components.

(1) Atmospheric Leach

In this system the calcined clay is mixed with an acid solution containing recycled dissolved aluminum chloride. Acid contents range from approximately 26% in the first stage to 1.5% in the final stage at boiling point. Material concerns here are corrosive attack by the $HCl/AlCl_3 \cdot 6H_2O$ solution associated with abrasive particles during leaching.

- Candidate Materials

- Leach Tanks: Carbon steel - polymeric contact lining plus acid resistant brick interfacing the leach liquids. Titanium metal for exposed parts.

- Flash Tanks: Carbon steel - polymeric contact lining plus acid resistant brick.

- Condensers: Karbate heads, tubes; or titanium

(2) Iron Removal

This system has the requirement for solvent addition which adds further complication to materials selection. Rubber material and certain polymers experience early failure in this media. An additional factor is the planned changing of the iron to the ferric state by addition of free chlorine.

$Fe^{++} + 1/2\ Cl_2 \longrightarrow Fe^{+++} + Cl^-$. The metal chloride increases corrosivity uncertainties of the process fluids.

- Candidate Materials

  Generally, FRP materials can be used throughout this system. Titanium alloys can be considered for exposed metal applications. The plastic materials used in the FRP layups would be selected on the basis of test results.

(3) Evaporation

The evaporation stage will require containment of HCl liquids and vapors. A wide range of concentrations will be present.

In areas of this system where temperatures are 180°F or less, rubber-lined components will be used for pressure vessels, etc. Ceramic liners, and possibly Kynar or Teflon may be used in those regions over 180°F. Circulating heaters and feed preheaters will use rubber-lined carbon steel shells and baffles, Karbate for tubing. Other materials which can be used are Kynar, Teflon, and alloys of Zirconium and Titanium.

(4) Crystallization

Continuing research program effort is necessary to provide data for selection of an optimum material for application in the sparging crystallizer. A review of existing data shows semi-hard rubber to be acceptable; however, long-term data is lacking and short-term data indicates some volume change in 43 day samples. Uncoated metals would be expected to have definite life limitations in regions wherein crystal content would provide abrasive damage. Materials for use in equipment such as centrifuges, pumps, and slurry piping will require evaluation on an item-to-item basis dependent upon product liquid and solids content. Zirconium alloys and rubber-clad wetted parts are candidates for centrifuge and pump components. Resiliency to abrasive particulates give rubber or elastomeric materials an advantage in this service.

(5) Decomposition

The decomposition stages impose severe environmental conditions on the construction materials.

The first stage decomposer vessels can be adequately designed using carbon or alloy steels lined with high alumina refractories. For the following decomposer stages wherein higher temperatures are encountered, the vessel or liner would probably require the use of high alloy materials such as an Inconel or Hastelloy to be the base metal or substrate for a refractory lining. The application of properly selected insulation brick materials to keep temperatures below 150°F at the metal liner would allow polymeric lining materials to be selected.

The heat exchange portion of the first stage decomposer wherein temperatures would be in the 350°F - 550°F range would utilize Inconel 625 or other high alloy metals for tubing.

The final stage direct-fired fluid-bed decomposer will experience temperatures which approximate 1,800°F. The working environment would dictate the use of refractory materials in contact with the hot gases and product. High aluminum oxide refractories are a prime candidate for this service. Important design considerations should include the selection of adequate materials for liner attachments, and orifice plates.

Material selection throughout the decomposer sections must include the added requirement that any corrosion product formed or removed from contacting surfaces will not harmfully contaminate the product alumina.

### 4.2.8 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:

| | % |
|---|---|
| $SiO_2$ | 46.4 |
| $Al_2O_3$ | 36.5 |
| L.O.I. | 13.54 |
| $TiO_2$ | 2.23 |
| $Fe_2O_3$ | 0.86 |
| MgO | 0.082 |
| CaO | 0.042 |
| $K_2O$ | 0.095 |
| $Na_2O$ | 0.046 |
| $SO_4^{=}$ | 0.10 |
| $P_2O_5$ | 0.069 |
| $F^-$ | 0.022 |
| Other | 0.04 |
| TOTAL | 100.0 |

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

(4) Entering clay is calcined by means of fluidized solids techniques with direct powered coal firing as the heat source.

(5) There is a 1% dust loss (calcined basis) from the 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. The 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) 0.56% of the calcined clay is soluble in leach in the form of impurities.

(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 and HCl from leach 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 0.1% HCl.

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

(22) The organic make-up in solvent extraction is assumed to be 1 ton/d.

(23) Calcined clay equivalent to 150% of stoichiometric $Al_2O_3$ requirements is used to treat the $FeCl_3$ strip liquor.

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

(25) 0.2 lb of 35% acid wash is used per 1 lb of $AlCl_3 \cdot 6H_2O$ crystals.

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

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

(28) The bleed liquor is stripped to remove 94% of free HCl and evaporated to a 45% solution of chlorides.

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

(30) A sufficient quantity of $H_2SO_4$ is added before the waste chlorides decomposition to discharge Na, K, Ca, and Mg as sulfates. Al is discharged as $Al_2O_3$.

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

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

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Table 4-2-2 (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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | *amb. | amb. | 150 | 150 | 120 | 115 | amb. | 250 | 140 | 135 | 135 |
| **Component** | | | | | | | | | | | |
| $Al_2O_3$ | 1097 | 1097 | 1086 | 1086 | | | | 11 | 53 | | |
| $AlCl_3$ | | | | | | 429 | | | 3072 | 2261 | 3089 |
| $AlCl_3 \cdot 6H_2O$ | | | | | | | | | | | |
| $Fe_2O_3$ | 25 | 25 | 25 | 25 | | | | | 1 | | |
| $FeCl_3$ | | | | | | | | | 47 | 35 | 48 |
| HCl | | | | | | 2322 | | | 111 | 82 | 111 |
| L.O.I. | 407 | 407 | | | | | | 407 | | | |
| $H_2O$ | 683 | 683 | | | 3741 | 6609 | 5 | 683 | 7156 | 5267 | 8779 |
| Other | 81 | 81 | 96 | 96 | | | | 1 | 80 | | |
| Other as Soluble Salts | | | | | | 192 | | | 213 | 157 | 210 |
| $SiO_2$ | 1395 | 1395 | 1381 | 1381 | | | | 14 | 1352 | 7 | 8 |
| Organic | | | | | | | | | | | |
| $H_2SO_4$ | | | | | | | | | | | |
| $Cl_2$ | | | | | | | | | | | |
| Total | 3688 | 3688 | 2588 | 2588 | 3741 | 9552 | 5 | 1116 | 12085 | 7809 | 12245 |

All units are in short tons per day

*amb.: ambient

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Table 4-2-2 (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 | 16 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 135 | 135 | 130 | 120 | 160 | 160 | 120 | 130 | 140 | 160 |
| **Component** | | | | | | | | | | |
| $Al_2O_3$ | 53 | | | | | | 61 | | | |
| $AlCl_3$ | 811 | 828 | 3088 | 3078 | 3111 | 433 | 32 | 1 | | 429 |
| $AlCl_3 \cdot 6H_2O$ | | | | | | 4843 | | | 60 | |
| $Fe_2O_3$ | 1 | | | | | | 25 | | | |
| $FeCl_3$ | 12 | 13 | 48 | | | | | | | |
| HCl | 29 | 29 | 121 | 121 | 107 | 1890 | 1 | | 2 | 1949 |
| L.O.I. | | | | | | | | | | |
| $H_2O$ | 1889 | 3512 | 8779 | 8779 | 6990 | 4825 | 3138 | 5 | 4 | 4948 |
| Other | 80 | | | | | | 82 | | | |
| Other as Soluble Salts | 56 | 53 | 210 | 210 | 210 | 210 | 3 | | | 192 |
| $SiO_2$ | 1345 | 1 | | | | | 1373 | 8 | | |
| Organic | | | | | | | 1 | | | |
| $H_2SO_4$ | | | | | | | | | | |
| $Cl_2$ | | | | | | | | | | |
| Total | 4276 | 4436 | 12246 | 12188 | 10418 | 12201 | 4716 | 14 | 66 | 7518 |

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Table 4-2-2 (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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 150 | 250 | 500 | 150 | 250 | amb. | amb. | 500 | 500 | 500 | 140 |
| **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 | 511 |
| L.O.I. | | | | | | | | | | | |
| $H_2O$ | 163 | | | | 132 | 80 | 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 | 80 | 52 | 3837 | 1489 | 2348 | 511 |

Table 4-2-2 (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 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 140 | 140 | amb. | 80 | 90 | 115 | 140 | 255 | 255 | 255 | 255 |
| **Component** | | | | | | | | | | | |
| $Al_2O_3$ | | | | | | | | | | | |
| $AlCl_3$ | | | | | | 4 | | | 155 | 151 | 4 |
| $AlCl_3 \cdot 6H_2O$ | | | | | | | | | | | |
| $Fe_2O_3$ | | | | | | | | | | | |
| $FeCl_3$ | | | | | | | | | | | |
| HCl | 1272 | 1783 | 27 | 352 | 129 | 203 | 190 | 13 | 13 | | |
| L.O.I. | | | | | | | | | | | |
| $H_2O$ | | | | 655 | 512 | 365 | 4 | 335 | 1344 | 983 | 26 |
| Other | | | | | | | | | | | |
| Other as Soluble Salts | | | | | | 17 | | | 660 | 643 | 17 |
| $SiO_2$ | | | | | | | | | | | |
| Organic | | | | | | | | | | | |
| $H_2SO_4$ | | | | | | | | | | | |
| $Cl_2$ | | | | | | | | | | | |
| Total | 1272 | 1783 | 27 | 1007 | 641 | 589 | 194 | 348 | 2172 | 1777 | 47 |

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

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

| Process Stream | 55 | 56 | 57 | 58 | 69 | 70 | 72 | 87a |
|---|---|---|---|---|---|---|---|---|
| Temperature, °F | 255 | 255 | amb. | amb. | 160 | 80 | 80 | 80 |
| **Component** | | | | | | | | |
| $Al_2O_3$ | 2 | | | | | | | |
| $AlCl_3$ | | | | | | | | |
| $AlCl_3 \cdot 6H_2O$ | | | | | | | | |
| $Fe_2O_3$ | | | | | | | | |
| $FeCl_3$ | | | | | | | | |
| HCl | | 12 | | | 16 | | 29 | 1 |
| L.O.I. | | | | | | | | |
| $H_2O$ | | 32 | | 6 | 1820 | 1756 | 399 | 1020 |
| Other | 4 | | | | | | | |
| Other as Soluble Salts | 15 | | | | | | | |
| $SiO_2$ | | | | | | | | |
| Organic | | | | | | | | |
| $H_2SO_4$ | | | 12 | | | | | |
| $Cl_2$ | | | | | | | | |
| Total | 21 | 44 | 12 | 6 | 1836 | 1756 | 428 | 1021 |

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

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

| Process Stream | 89a | 89 | 90 | 91 | 92 | 102 | 111 | 112 | 113 | 114 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature, °F | amb. | 120 | 120 | 210 | 120 | 80 | amb. | 150 | amb. | amb. |
| **Component** | | | | | | | | | | |
| $Al_2O_3$ | | | | 8 | | | | 23 | | |
| $AlCl_3$ | | | 10 | 49 | 10 | | | | | |
| $AlCl_3 \cdot 6H_2O$ | | | | | | | | | | |
| $Fe_2O_3$ | | | | 24 | | | | 1 | | |
| $FeCl_3$ | | 6 | 54 | 1 | 48 | | | | | |
| HCl | | | | 1 | 1 | 6 | | | | 1 |
| L.O.I. | | | | | | | | | | |
| $H_2O$ | | | | 1020 | 1020 | 19 | | | | |
| Other | | | | 2 | | | | 2 | 16 | |
| Other as Soluble Salts | | | | | | | | | | |
| $SiO_2$ | | | | 29 | | | | 29 | | |
| Organic | 1 | 3081 | 3082 | 1 | | | | | | |
| $H_2SO_4$ | | | | | | | | | | |
| $Cl_2$ | | | | | | | 10 | | | |
| Total | 1 | 3087 | 3146 | 1135 | 1079 | 25 | 10 | 55 | 16* | 1 |

*Coal ash component of fuel (for material balance purposes only)

### 4.2.9 EQUIPMENT LIST

ALUMINA FROM CLAY VIA HYDROCHLORIC ACID EXTRACTION - HCl PRECIPITATION PROCESS

Clay Preparation Area

Truck Dump Hopper (4) - 70 ton receiving hopper of fabricated steel with vertical support legs. (1 spare)

Truck Dump Wobbler Feeder (4) - 350 ton/h, 60 in wide x 18 bar, 11 1/2 in pitch series with 2 in openings between bars. (1 spare)

Under Wobbler Feeder Belt Conveyor (4) - 350 ton/h (1 spare)

Primary Crushers and Chutes (4) - 350 ton/h double roll crushers, feed size - 12 in, product size - 2 in.(1 spare)

Primary Crusher Belt Conveyor (4) - 350 ton/h. (1 spare)

Stockpile Distributor Belt Conveyor (1) - 1,000 ton/h

Stockpile Enclosure (1) - 100,000 ton capacity, 200 ft x 600 ft, A-frame steel building

Stockpile Reclaim Hoppers (2) - 25 ton capacity. (1 spare)

Stockpile Wobbler Feeder (2) -270 ton/h,60 in wide x 18 bar, 9 in pitch series with 3/4 in openings between bars. (1 spare)

Secondary Crusher Feed Belt Conveyor (2) - 300 ton/h

Secondary Crushers and Chutes (3) - 150 ton/h hammermill, 2 in feed size, minus 3/4 in product size. (1 spare)

Secondary Crusher Discharge Belt Conveyor (2) - 300 ton/h

Secondary Crusher Bucket Elevator (2) - 250 ton/h

Secondary Crushing Screens and Chutes (3) - 150 ton/h, plus 3/4 in oversize, minus 20 mesh undersize. (1 spare)

EQUIPMENT LIST (Cont)

Roll Compactors (4) - 35 ton/h,10 in dia x 36 in, minus 20 mesh feed size, 3/4 in product size. (1 spare)

Roll Compactors Recirculation Belt Conveyor (1) - 100 ton/h

Raw Clay Surge Bin Feed Belt Conveyor (1) - 30 ton/h

Raw Clay Surge Bin (1) - 1,000 ton capacity, 24 ft dia x 73 ft str. side

Raw Clay Weighfeeders (2) - 150 ton/h

Calciner Feed Belt Conveyor (2) - 150 ton/h

Clay Calciner System (Fluid-Bed) (2) - 3 stage fluidized bed dryer with air heater - 19 in dia calciner - primary cooler followed by a secondary cooler for 135 ton/h feed and 95 ton/h product. Gas scrubber included

Coal Pulverizers (4) -2 units - 5 ton/h, 2 units 2.5 ton/h at 20 mesh size

Calciner Discharge Apron Feeder (2) - 95 ton/h

Calcine Bucket Elevator (2) - 190 ton/h. (1 spare)

Calcine Vibrating Screen (3) - 100 ton/h, 20 mesh screen

Cage Mill Grinder (2) - 150 ton/h, 2-roll 60 in dia grinder, 20 mesh product size. (1 spare)

Cage Mill Discharge Belt Conveyor (2) - 200 ton/h. (1 spare)

Storage Bin Bucket Elevator (2) - 200 ton/h. (1 spare)

Calcined Clay Storage Bins (2) - 1,500 ton capacity, 30 ft dia x 88 ft str. side

Calcine Weighfeeders (4) -200 ton/h. (2 spares)

EQUIPMENT LIST (Cont)

Leach Tank Feed Conveyors (2) - 125 ton/h

Chutes and Hoppers

Dust Collection System-Bag houses with piping, blowers, and controls

Leaching, Thickening, CCD Washing, and Filtration Area

Leach Tank Screw Feeders (4) - 81 ton/h, totally sealed feeders, rubber-lined carbon steel construction. (2 spares)

Leach Tanks (8) - 16 ft dia x 26 ft str. side constructed of carbon steel shell with polymeric membrane and acid-resistant brick lining. (2 trains)

Leach Tank Condenser (4) - 1,000 $ft^2$ heat transfer area. Impervious graphite heads and tubes, carbon steel shell. (2 spares)

Leach Tank Recirculation Pumps (8) - 1,000 gal/min fluoropolymer-lined cast iron construction. (4 spares)

Condensate Pumps (4) - 100 gal/min, fluoropolymer-lined cast iron construction. (2 spares)

Flash Tanks (2) - 11 ft dia x 11 ft str. side constructed of carbon steel shell with polymeric membrane and acid-resistant brick lining

Flash Tank Vapor Condensers (4) - 5,500 $ft^2$ heat transfer area. Impervious graphite heads and tubes, carbon steel shell

Condensate Tanks (2) - 60,000 gal, 22 ft dia x 24 str. side. Rubber-lined carbon steel construction with steam ejectors

Leach Slurry Pumps (4) - 1,500 gal/min, fluoropolymer-lined cast iron construction.(2 spares)

Dilute HCl Transfer Pumps (4) - 200 gal/min, rubber-lined cast iron construction. (2 spares)

EQUIPMENT LIST (Cont)

Leach Tank Agitators (8) - butyl-lined carbon steel construction

Sand Thickener Tanks (5) - 106 ft dia x 15 ft str. side. Carbon steel shell, covered and rubber-lined. Four units operating in parallel. (1 spare)

Sand Thickener Rake Mechanisms (5) - two-arm rakes, rubber-lined carbon steel construction. (1 spare)

Sand Thickener Underflow Pumps (10) - 200 gal/min, rubber-lined cast iron construction. (5 spares)

Sand Thickener Overflow Pumps (10) - 610 gal/min, rubber-lined cast iron construction. (5 spares)

Sand Washer Tanks (18) - 106 ft dia x 15 ft str. side, carbon steel shell, covered and rubber-lined. (2 trains - 9 unit CCD washing)

Sand Washer Rake Mechanisms (18) - two-arm rakes, rubber-lined carbon steel construction

Sand Washer Underflow Pumps (36) - 920 gal/min, rubber-lined cast iron construction. (18 spares)

Sand Washer Overflow Pumps (36) - 1,030 gal/min, rubber-lined cast iron construction. (18 spares)

Waste Tank (1) - 45,000 gal, 17 ft dia x 24 ft str. side, rubber-lined steel shell

Sand Slurry Pumps (2) - 2,750 gal/min, rubber-lined cast iron construction. (1 spare)

Flocculant Preparation System ($HNO_3$) (1) - includes hoppers, feeders, mix tank and agitator, transfer pumps, storage tank, and solution pumps

EQUIPMENT LIST (Cont)

Filter Presses and Repulpers (5) - 2,900 $ft^2$ retractable shell filter. 815-gal/min feed with polypropylene leaves and all wetted parts of rubber-lined carbon steel or titanium. (2 spares)

Press Cake Relay Tank (2) - 4,600 gal, 10 ft dia x 8 ft str. side. Rubber-lined carbon steel construction

Repulped Slurry Pumps (4) - 200 gal/min, rubber-lined cast iron construction. (2 spares)

Vibrating Screens (2) - 4 1/2 ft x 5 1/2 ft polypropylene construction

Collecting Sluice (1) - rubber-lined carbon steel construction

Spent Filter Aid Dumpers (4) - portable bins

Filtrate Surge Tanks (2) - 235,000 gal, 36 ft dia x 32 ft str. side, rubber-lined carbon steel construction

Filtrate Pumps (4) - 2,500 gal/min, rubber-lined cast iron construction. (2 spares)

Filter Aid Preparation System ($HNO_3$) (1) - includes storage tank, conveyor, weighfeeder, slurry tanks and agitators, slurry pumps, and liquor pumps

In-line Chlorine Blender (2) - chlorine gas pipeline blender

Iron Removal, $FeCl_3$ Stripping, $FeCl_3$ Conversion Area

Solvent Surge Tank (1) - 65,000 gal, 22 ft dia x 24 ft str. side, FRP-lined carbon steel construction

Solvent Surge Tank Pumps (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Head Tanks (8) - 2,000 gal, FRP construction

## EQUIPMENT LIST (Cont)

Mixer-Settlers (12) - 65 ft x 20 ft x 10 ft deep concrete tanks with FRP lining

Mixer-Settlers Covers (12) - segmented self-supporting FRP construction

Loaded Solvent Pumps (4) - 1,000 gal/min, 316 stainless steel construction. (2 spares)

Mixing Pumps (10) - 316 stainless steel construction

Mixing Pump Baffles (10) - FRP construction

Raffinate Pumps (4) - 2,400 gal/min, rubber-lined carbon steel construction. (2 spares)

Raffinate Surge Tank (1) - 235,000 gal, 36 ft dia x 32 ft str. side, FRP-lined carbon steel construction

Raffinate Storage Transfer Pumps (2) - 2,400 gal/min, rubber-lined carbon steel construction. (1 spare)

Loaded Solvent Surge Tank (1) - 65,000 gal, 22 ft dia x 24 ft str. side, FRP-lined carbon steel construction

Loaded Solvent Surge Transfer Pumps (2) - 1,000 gal/min, 316 stainless steel construction. (1 spare)

Regenerated Solvent Pumps (4) - 1,000 gal/min, 316 stainless steel construction. (2 spares)

Wash Water Tanks (2) - 15,000 gal, 13.5 ft dia x 17 ft str. side, FRP construction

Wash Water Tank Pumps (4) - 260 gal/min, rubber-lined cast iron construction. (2 spares)

Spent $FeCl_3$ Pumps (4) - 260 gal/min, rubber-lined cast iron construction. (2 spares)

EQUIPMENT LIST (Cont)

$FeCl_3$ Liquor Surge Tank (1) - 40,000 gal, 20 ft dia x 23 ft str. side, FRP-lined carbon steel construction

$FeCl_3$ Liquor Surge Tank Pump (2) - 260 gal/min, rubber-lined cast iron construction. (1 spare)

Decanol Unloading Pump (1) - 400 gal/min, cast iron construction

Decanol Storage Tank (1) - 5,500 gal, 10 ft dia x 12 ft str. side, carbon steel construction

Decanol Blending Pumps (2) - 250 gal/min, cast iron construction. (1 spare)

Kerosene Unloading Pump (1) - 400 gal/min, cast iron construction

Kerosene Storage Tank (1) - 5,500 gal, 10 ft dia x 12 ft str. side, carbon steel construction

Kerosene Blending Pump (2) - 250 gal/min, cast iron construction. (1 spare)

Alamine Unloading Pump (1) - 400 gal/min, cast iron construction

Alamine Storage Tank (1) -5,500 gal, 10 ft dia x 12 ft str. side, carbon steel construction

Alamine Blending Pump (2) - 250 gal/min, cast iron construction. (1 spare)

Solvent Blend Tank (1) - 4,000 gal, 7 ft dia x 15 ft str. side, carbon steel construction

Solvent Blend Tank Agitator (1) - thorough agitation. 304 stainless steel construction

12.5 Ton Load Cell (1) - 6 h cycle to fill, agitate, and empty

EQUIPMENT LIST (Cont)

Solvent Make-up Pumps (2) - 40 gal/min, cast iron construction. (1 spare)

Calcined Clay Conveyor (1) - pneumatic system with 28 ton/h capacity at 80 lb/ft$^3$ with blower package, 6-in conveying line, surge hopper, binvents, and fan. Carbon steel construction

Calcined Clay Surge Bin (1) - 350 ft$^3$ capacity, 8 ft dia x 6 ft str. side carbon steel construction

Reactor Feed Conveyor (1) - 3.5 ton/h, rubber-lined

$FeCl_3$ Digestion Reactors (3) - 10,000 gal, 12 ft dia x 15 ft str. side, carbon steel shell, rubber membrane, and acid brick lining

Digestion Reactor Agitators (3) - butyl rubber-lined carbon steel construction

Digestion Reactor Steam Heaters (3) - 1-in steam coils for 3.8 x 10$^6$ Btu/h heat transfer service. Inconel 625 construction

Condensed Vapor Pump (2) - 60 gal/min, fluoropolymer-lined cast iron construction. (1 spare)

Digestion Slurry Surge Tank (1) - 60,000 gal, 22 ft dia x 23 ft str. side, rubber-lined carbon steel construction

Digestion Slurry Surge Tank Pumps (2) - 290 gal/min, fluoropolymer-lined cast iron construction. (1 spare)

Digestion Slurry Surge Tank Agitator (1) - 100% solid suspension, rubber-lined carbon steel construction

Pregnant Liquor Evaporation, $AlCl_3 \cdot 6H_2O$ Crystallization, and Centrifuging Area

Pregnant Liquor Evaporators (5) - single effect systems in parallel operation consisting of 25 ft dia x 20 ft str. side

## EQUIPMENT LIST (Cont)

evaporator with demister pad, vapor and circulating piping, and barometric condenser with 2-stage ejector system. Evaporation rate = 750 ton/d of $H_2O$. Total connected, horsepower is 700 hp and steam requirements are 1,000 lb/h at 100 psig. Constructed of rubber-lined carbon steel

Feed Liquor Preheaters (2) - 2,500 $ft^2$ heat transfer area. Impervious graphite heads and tubes, carbon steel shell

Liquor Circulating Heaters (5) - 10,000 $ft^2$ heat transfer area. Impervious graphite heads and tubes, rubber-lined carbon steel shell

Liquor Circulating Pumps (10) - 15,000 gal/min, rubber-lined cast iron construction. (5 spares)

Evaporator Transfer Pumps (10) - 600 gal/min, rubber-lined cast iron construction. (5 spares)

Evaporator Hotwell (1) - 12 ft x 20 ft x 8 ft, FRP-lined concrete with segmented self-supporting FRP cover complete with scrubber for vent gas

Evaporator Hotwell Pumps (2) - 10,500 gal/min, rubber-lined cast iron construction. (1 spare)

Evaporator Cooling Tower (1) - 11,000 gal/min (10 wt % HCl) capacity from 130°F to 80°F with an evaporation rate of 240,000 lb/h single-cell cross-flow tower 66 ft x 42 ft with one 225-hp fan. Drift loss = 0.008% of circulating liquid. Tower with 5-stage scrubber to reduce HCl in vapor to 1.5 ppm. Tower constructed of FRP, spray bars and nozzles of PVC

Cooling Tower Sumps (4) - 15 ft x 18 ft x 8 ft, acid brick-lined concrete

Spray Scrubber Pumps (2) - 2,000 gal/min, rubber-lined cast iron construction. (1 spare)

EQUIPMENT LIST (Cont)

Cooling Tower Transfer Pumps(2) - 10,000 gal/min rubber-lined cast iron construction. (1 spare)

2-Stage Crystallizers (3) - 200,000 lb/h $AlCl_3 \cdot 6H_2O$ crystals capacity. 36 ft dia x 26 ft str. side crystal suspension containers with central pipes, circulating piping, and coolant circulating piping all fabricated of rubber-lined carbon steel. Also included are two heat exchangers with 5,400 $ft^2$ of heat transfer surface constructed of impervious graphite heads and tubes and carbon steel shell

Coolant Circulating Pumps (12) - 4,400 gal/min, rubber-lined cast iron construction. (6 spares)

1st Stage Crystallizer Product Pumps (6) - 1,360 gal/min rubber-lined cast iron construction. (3 spares)

2nd Stage Crystallizer Product Pumps (6) - 1,000 gal/min rubber-lined cast iron construction. (3 spares)

Emergency Storage Falling Film Absorbers (4) - 1,500 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell

Emergency Storage Absorption Towers (4) - 11 ft dia x 25 ft str. side with 1,425 $ft^3$ of 2 in ceramic packing. Constructed of carbon steel shell, lined with acid-resistant brick with a polymeric membrane

Emergency Storage Tanks (6) - 230,000 gal, 35 ft dia x 32 ft str. side, rubber-lined carbon steel construction with 1 ft dia x 6 ft high vent scrubber

Emergency Storage Reboilers (4) - 400 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell construction

Emergency Storage Pumping System (6) - 3,000 gal/min, rubber-lined cast iron construction

EQUIPMENT LIST (Cont)

1st Stage Crystallizer Product Centrifuges (4) - 51 ton/h two-stage pusher type. Constructed of rubber-lined carbon steel housing, Hastelloy process contact parts and titanium screens. Horsepower requirements are 100 hp for basket, 60 hp for push plate. (1 spare)

1st Stage Centrate Tanks (3) - 10,000 gal, 10 ft dia x 18 ft str. side, rubber-lined carbon steel construction

2nd Stage Crystallizer Product Centrifuges (4) - 51 ton/h two stage pusher type. Constructed of rubber-lined carbon steel housing, Hastelloy process contact parts and titanium screens. Horsepower requirements are 100 hp for basket, 60 hp for push plate. (1 spare)

2nd Stage Centrate Tanks (3) - 7,000 gal, 10 ft dia x 12 ft str. side, rubber-lined carbon steel construction

Hydrocyclones (8) - 24 in dia handling a flow of 460 gal/min with a sp. gr. differential of 1.7. Rubber-lined carbon steel construction

1st Stage Centrifuge Wash Acid Tank (3) - 3,000 gal, 8 ft dia x str. side, rubber-lined carbon steel construction

1st Stage Centrate Pumps (6) - 1,000 gal/min, rubber-lined cast iron construction. (3 spares)

2nd Stage Centrate Pumps (6) - 650 gal/min, rubber-lined cast iron construction. (3 spares)

Centrifuge Wash Acid Pumps (6) - 300 gal/min, rubber-lined cast iron construction. (3 spares)

Crystal Bins (3) - 36,000 $ft^3$, 36 ft dia x 36 ft str. side. Bulk density = 83 $lb/ft^3$. Rubber-lined carbon steel construction

Crystal Weighfeeders (3)-110 ton/h capacity, bulk density = 83 lb/$ft^3$ rubber-lined carbon steel construction

EQUIPMENT LIST (Cont)

Recycle Crystal Slurry Tank (1) - 200 gal, 3 ft dia x 4 ft str. side, rubber-lined carbon steel construction

Recycle Crystal Slurry Tank Agitator (1) - rubber-lined carbon steel construction. Exposed metal to be zirconium-clad carbon steel

Recycle Crystal Slurry Pumps (2) - 20 gal/min, rubber-lined cast iron construction. (1 spare)

1st Stage Centrifuge Conveyors (3) - 55 ton/h, bulk density of 83 $lb/ft^3$. Gas-tight, rubber-lined carbon steel construction

2nd Stage Centrifuge Conveyors (3) - 55 ton/h, bulk density of 83 $lb/ft^3$. Gas-tight, rubber-lined carbon steel construction

Crystal Conveyors to Decomposers (3) - 110 ton/h, bulk density of 83 $lb/ft^3$. Gas-tight, rubber-lined carbon steel construction

Centrifuge Discharge Transfer Conveyors (3) - 110 ton/h, bulk density of 83 $lb/ft^3$. Gas-tight, rubber-lined construction

$AlCl_3 \cdot 6H_2O$ Decomposition Area

Decomposer Feed Screw Conveyors (4) - 60 ton/h of Aluminum Chloride Hexahydrate crystals at 83 $lb/ft^3$. Gas-tight, rubber-lined carbon steel construction

Decomposer Flash Dryers (4) - 6 ft dia x 70 ft str. side, constructed of carbon steel shell, polymeric membrane, castable refractory, and brick lining

Decomposer Flash Dryer Cyclones (4) - 10 ft dia x 20 ft str. side, constructed of carbon steel shell, polymeric membrane, castable refractory and brick lining

Indirect Fired Fluid Bed Decomposers (2) - 21 ft dia x 30 ft str. side, constructed of carbon steel shell, polymeric membrane, castable refractory, and brick lining. Includes Inconel 625 distributor plate and heating coils (2) - 2,585 x 10 ft long heat tubes of finned 1 in diameter pipes of Inconel 625 construction

EQUIPMENT LIST (Cont)

Indirect Fired Decomposer Cyclones (2) - 10 ft dia x 16 ft str. side, constructed of carbon steel shell, polymeric membrane, castable refractory, and brick lining

Indirect Fired Decomposer Gas Cooler (4) - 1,375 $ft^2$ heat transfer surface. Carbon steel shell and tube construction

Indirect Fired Decomposer Gas Blower (3) - 18,400 SCFM capacity at 14.7 psia suction pressure and 300°F suction temperature. Discharge pressure is 20.7 psia. (1 spare)

Indirect Fired Decomposer Product Hoppers (2) - carbon steel construction

Indirect Fired Decomposer Heating System (3) - 200 x $10^6$ Btu/h Dowtherm "A" heating system including coal pulverizer, coal feed hoppers, feed system, combustion air blower, fluidized bed combustor with start-up system, Dowtherm coils, cyclone collector, air preheater, circulating pumps, flash tanks, expansion tanks, and temperature controls

Waste Heat Boilers and Recycle Gas Heaters (3) - capacity of 85,000 lb/h of 100-psig steam supplied with 350,000 lb/h of 1,300°F waste gas

Heating System Coal Pulverizers (3) - 11.5 ton/h at 20 mesh

Heating System Ash Handling (3) - 1.1-ton/h system with blowers, piping cyclone, and ash bin

Heating System $SO_2$ Scrubber (3) - 76,200 SCFM with vertical wet approach Venturi Scrubber, flooded elbows and cyclone separator capable of removing 99% of fly ash and dust and 96% of $SO_2$

Decomposer Flash Calciner (2) - 5 ft dia x 75 ft str. side, constructed of carbon steel shell, polymeric lining, castable refractory, and brick lining

Flash Calciner Cyclone (2) - 18 ft dia x 32 ft str. side, constructed of carbon steel shell, polymeric lining, castable refractory, and brick lining

EQUIPMENT LIST (Cont)

Direct Fired Calciner (2) - 20 ft dia x 30 ft str. side, constructed of carbon steel shell, polymeric lining, castable refractory, and brick lining. Includes Inconel 625 distributor plate. 32 ton/h product capacity

Direct Fired Calciner Cyclone (2) - 21 ft dia x 38 ft str. side, constructed of carbon steel shell, polymeric lining, castable refractory, and brick lining

Direct Fired Calciner Oil Burners (2) - no. 6 fuel oil burner system with air blowers, oil guns, and controls

Product Hopper and Rotary Valves (2) - 40 ton/h product capacity, product density = 60 $lb/ft^3$. Carbon steel construction

Fluid Bed Cooler (2) - 32 ton/h product capacity. Cooling medium is both air and water through cooling coils. Product to be cooled from 1,800$^{\circ}$F to 150$^{\circ}$F. Heated air is used for product calciner combustion air

Alumina Conveying System (2) - 40 ton/h pneumatic system with blower package, 8 in conveying line, surge hopper, binvents, and fan

Alumina Silos (2) - 7,500 ton capacity. 50 ft dia x 50 ft str. side with 60$^{\circ}$ cone bottom. Carbon Steel construction

Bleed Stream Crystallization and Centrifuging, HCl Stripping, Waste Chloride Evaporation and Decomposition Area

Bleed Stream Crystallizer (1) - 5 ft dia x 6 ft str. side suspension container with central pipe, circulating piping, and cooling circulating piping constructed of rubber-lined carbon steel. Included are two coolant circulating pumps (100 gal/min) of carbon steel construction

## EQUIPMENT LIST (Cont)

Bleed Stream Crystallizer Circulating Pumps (2) - 1,000 gal/min, zirconium clad wetted parts. (1 spare)

Bleed Stream Crystallizer Heat Exchanger (1) - 100 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell

Bleed Stream Crystallizer Product Pumps (2) - 80 gal/min, rubber-lined cast iron construction. (1 spare)

Bleed Stream Crystallizer Hydrocyclones (2) - 0.5 ft dia. unit handling a flow of 80 gal/min with a sp. gr. differential of 1.7. Rubber-lined carbon steel construction

Bleed Stream Crystallizer Centrifuges (3) - 3 ton/h, single stage pusher type. Constructed of rubber-lined cast steel housing, Hastelloy process contact parts. (1 spare)

Bleed Stream Crystallizer Centrate Tank (2) - 800 gal, 4.5 ft dia x 7 ft str. side, rubber-lined carbon steel construction

Bleed Stream Crystallizer Centrate Pumps (4) - 800 gal/min, rubber-lined cast iron construction. (2 spares)

Bleed Stream Crystallizer Crystal Slurry Bin (3) - 200 gal, 3 ft dia x 4 ft str. side, rubber-lined carbon steel construction. (1 spare)

Bleed Stream Stripping Column (1) - 8 ft dia x 25 ft str. side with 600 $ft^3$ of 2 in ceramic packing rings constructed of fluoropolymer-lined carbon steel shell

Bleed Stream Stripping Reboiler (1) - 1,000 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell

Bleed Stream Stripping Underflow Pumps (2) - 750 gal/min, fluoropolymer-lined cast steel construction. (1 spare)

Bleed Stream Direct Contact Evaporators (2) - 11.5 ft dia x 30 ft str. side with 1,700 $ft^3$ of 3 in ceramic packing rings, constructed of carbon steel shell with acid-resistant brick and rubber membrane or fluoropolymer lining

EQUIPMENT LIST (Cont)

Bleed Stream Evaporator Underflow Pumps (4) - 12 gal/min, fluoropolymer-lined cast steel construction. (2 spares)

Bleed Stream Decomposer (1) - 18 ft dia Mannheim coal-fired furnace lined with carbofrax brick

Bleed Stream Decomposer Waste Apron Feeder (1) - 30 ton/d, carbon steel constructon

Solid Waste Pit (1) - 10 ft x 10 ft x 8 ft, concrete construction

Solid Waste Pit Agitator (1) - 316 stainless steel construction

Solid Waste Pit Pumps (2) - 400 gal/min, rubber-lined cast iron construction. (1 spare)

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

Leach Acid Absorption Columns (4) - 13 ft dia x 48 ft high with 2,750 $ft^3$ of 2 in ceramic packing rings in 3 sections, distributors and collectors. Constructed of carbon steel shell with acid resistant brick lining with polymeric membrane

Intermediate Cooling Heat Exchangers (4) - 500 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell

Intermediate Cooling Recirculation Pumps (8) - 100 gal/min, fluoropolymer-lined cast steel construction. (4 spares)

Vapor Product Blowers (2) - 560 ton/d HCl gas and water vapor. Suction pressure is atmospheric and discharge pressure is 30 psig. Brake horsepower developed is 1,260 at 7,050 rpm. Housing constructed of cast steel and rotor of alloy steel. (1 spare)

Liquid Product Recirculation Pumps (8) - 2,300 gal/min, fluoropolymer-lined cast steel construction

EQUIPMENT LIST (Cont)

Wash Acid Falling Film Absorbers (4) - 1,500 $ft^2$ heat transfer surface. Constructed of impervious graphite heads and tubes, carbon steel shell

Wash Acid Falling Film Absorber Vapor Product Blowers (2) - 19.5 ton/d HCl gas and water vapor. Suction pressure is atmospheric and discharge pressure is 30 psig. Brake horsepower developed is 600 at 10,000 rpm. Housing contructed of cast steel and rotor of alloy steel. (1 spare)

Wash Acid Falling Film Absorber Liquid Product Pumps (4) - 62 gal/min, rubber-lined cast steel construction

Wash Acid Falling Film Absorber Liquid Product Heat Exchangers (4) - 400 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell construction

Wash Acid Absorption Towers (4) - 11 ft dia x 25 ft str. side with 1,425 $ft^3$ of 2 in ceramic packing. Constructed of carbon steel shell lined with acid resistant brick plus a rubber membrane or fluoropolymers

Wash Acid Absorption Towers Circulating Pumps (8) - 1,250 gal/min. fluoropolymer-lined cast steel construction. (4 spares)

HCl Storage Tanks (2) - 230,000 gal, 35 ft dia x 32 ft str. side, rubber-lined carbon steel construction

Air Padding for HCl Unloading (2) - 1 ft dia x 8 ft str. side, packed vent scrubber of FRP construction

HCl Solution Make-up Pumps (4) - 22 gal/min, rubber-lined cast steel construction. (2 spares)

Dilute Acid Gas Falling Film Absorbers (2) - 9,730 $ft^2$ heat transfer surface. Impervious graphite heads and tubes, carbon steel shell

Dilute Acid Gas Falling Film Absorber Product Pumps (4) - 166 gal/min, rubber-lined cast steel construction. (2 spares)

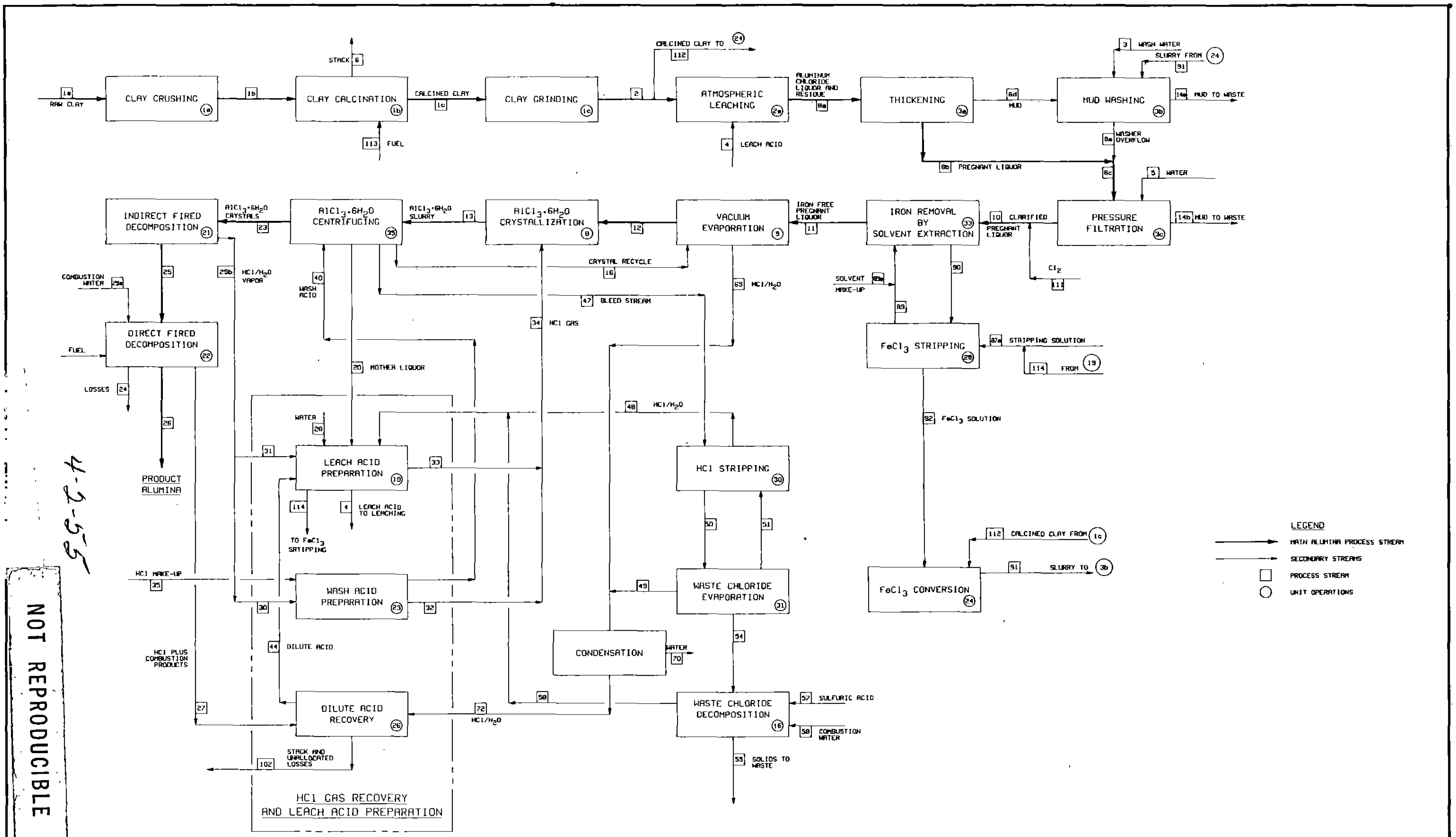
EQUIPMENT LIST (Cont)

Dilute Acid Gas Absorption Towers (2) - 7.5 ft dia x 25 ft str. side with 990 $ft^3$ of 2 in ceramic packing rings. Constructed of carbon steel shell with fluoropolymeric lining. Teflon pad demister included

Utilities

Steam Plant and Auxiliary Systems (1) - 150,000 lb/h coal-fired boiler, 125 psig saturated steam. Complete with controls, ash handling, fly ash and $SO_2$ scrubber, feed water and condensate system, and coal pulverizers

Cooling Towers and Auxiliary Systems (1) - 12,000 gal/min from 130°F to 90°F at 80°F ambient wet bulb temperature. Horsepower requirement is 250. Pumps and concrete basin are included




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

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

| NO. | DATE | REVISION | BY | 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

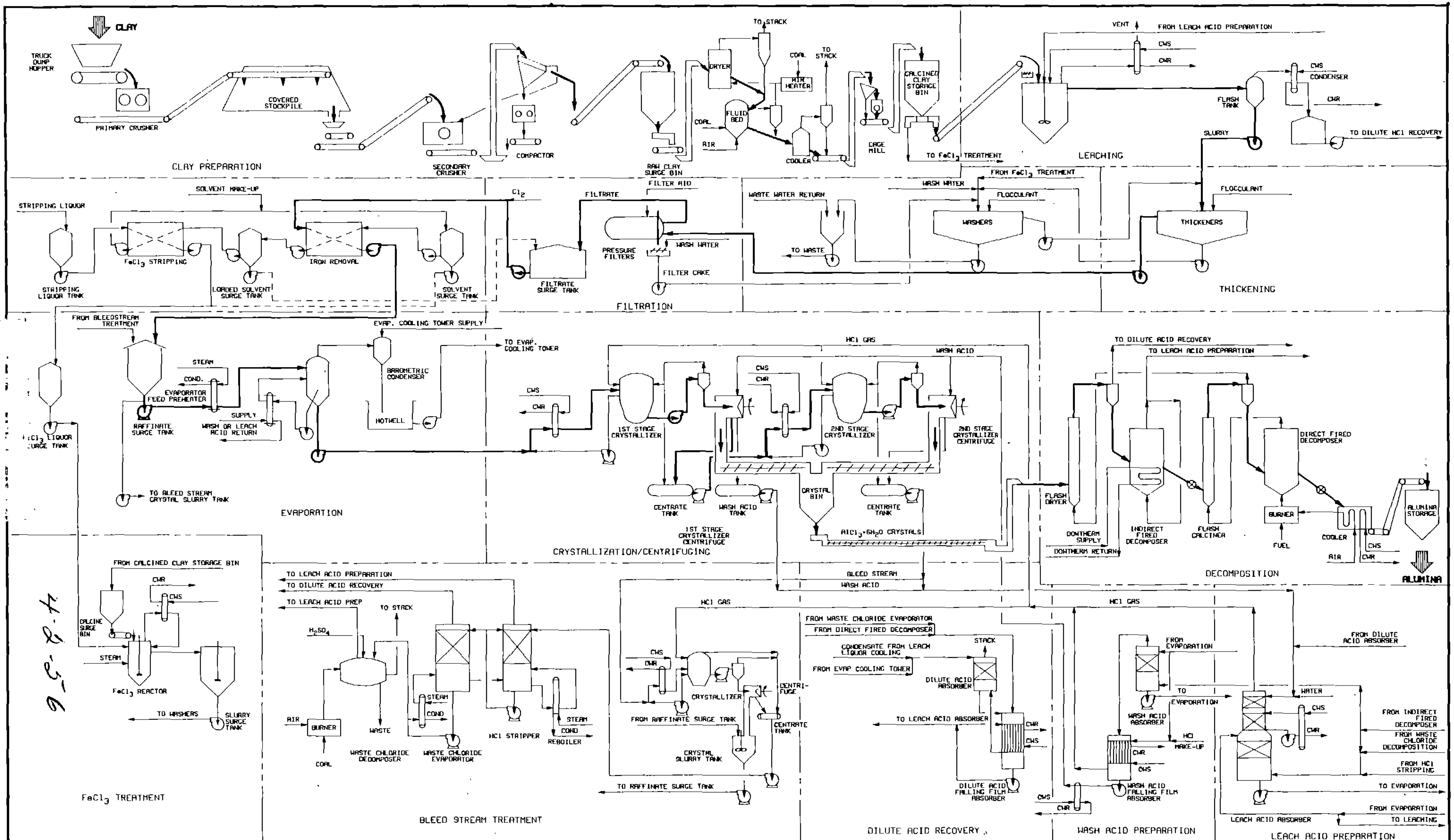
**KAISER ENGINEERS**

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

**ALUMINA FROM CLAY**
**HYDROCHLORIC ACID PROCESS**
**HCl GAS INDUCED CRYSTALLIZATION**

JOB No. 76161-002 | DWG. No. FIGURE NO. 4-2-2 | REVISION R-1

4-2-55




4-2-56

CWR - COOLING WATER RETURN
CWS - COOLING WATER SUPPLY
EQUIPMENT AS DEPICTED IN THIS DIAGRAM IS CONCEPTUAL AND IS PRESENTED FOR GRAPHICAL PURPOSES ONLY AND DOES NOT NECESSARILY REFLECT ACTUAL EQUIPMENT THAT MAY BE USED FOR THE PROCESS EITHER IN QUANTITY OR IN CONCEPT.
HEAVY LINE INDICATES MAIN STREAM.

| NO | DATE | REVISION | BY CHK | APP | APP | NOTES | DESCRIPTION | COST ACCOUNT |
|---|---|---|---|---|---|---|---|---|

CONSTRUCTION APPROVAL | APPROVAL | DATE | SCALE: NONE | DATE | PROFESSIONAL SEAL

DESIGNED BY / DRAWN BY / CHECKED BY / APPROVED BY / APPROVED BY

WORK COVERED BY THIS DRAWING CHARGED TO COST ACCOUNT ABOVE

**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 EXTRACTION-HCl GAS-INDUCED CRYSTALLIZATION PROCESS CONCEPT

JOB No. 76161-002 | DWG. No. FIG. NO. 4-2-3 | REVISION R-1

# 5. CONCLUSIONS AND RECOMMENDATIONS

The conclusion to be drawn from this study is that the clay/hydrochloric acid process incorporating HCl gas-induced crystallization has substantially lower capital and operating costs than the clay/nitric acid process.

The nitric acid process capital costs are estimated to be $214 per annual ton of production greater than the hydrochloric acid process. Operating costs for the nitric acid process are estimated to be $51 per ton of alumina greater than for the hydrochloric acid process.

The study shows that the clay/hydrochloric acid process using HCl gas-induced crystallization has the best economics of the six processes studied in Tasks 1 and 2 of this contract. The other five processes which have been studied are the hydrochloric acid/clay process using evaporative crystallization, a sulfurous acid/clay process, an anorthosite-lime sinter process, an alunite process, and the nitric acid/clay process.

Based on its superior economics, we recommend that the clay/hydrochloric acid process incorporating HCl gas-induced crystallization be used as the basis for the preliminary design of a 10-50 ton/d demonstration plant in Task 3 of this contract.

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APPENDIX A

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2. HCl Processing

3. HCl Properties

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APPENDIX B

## HEAT AND MASS BALANCES

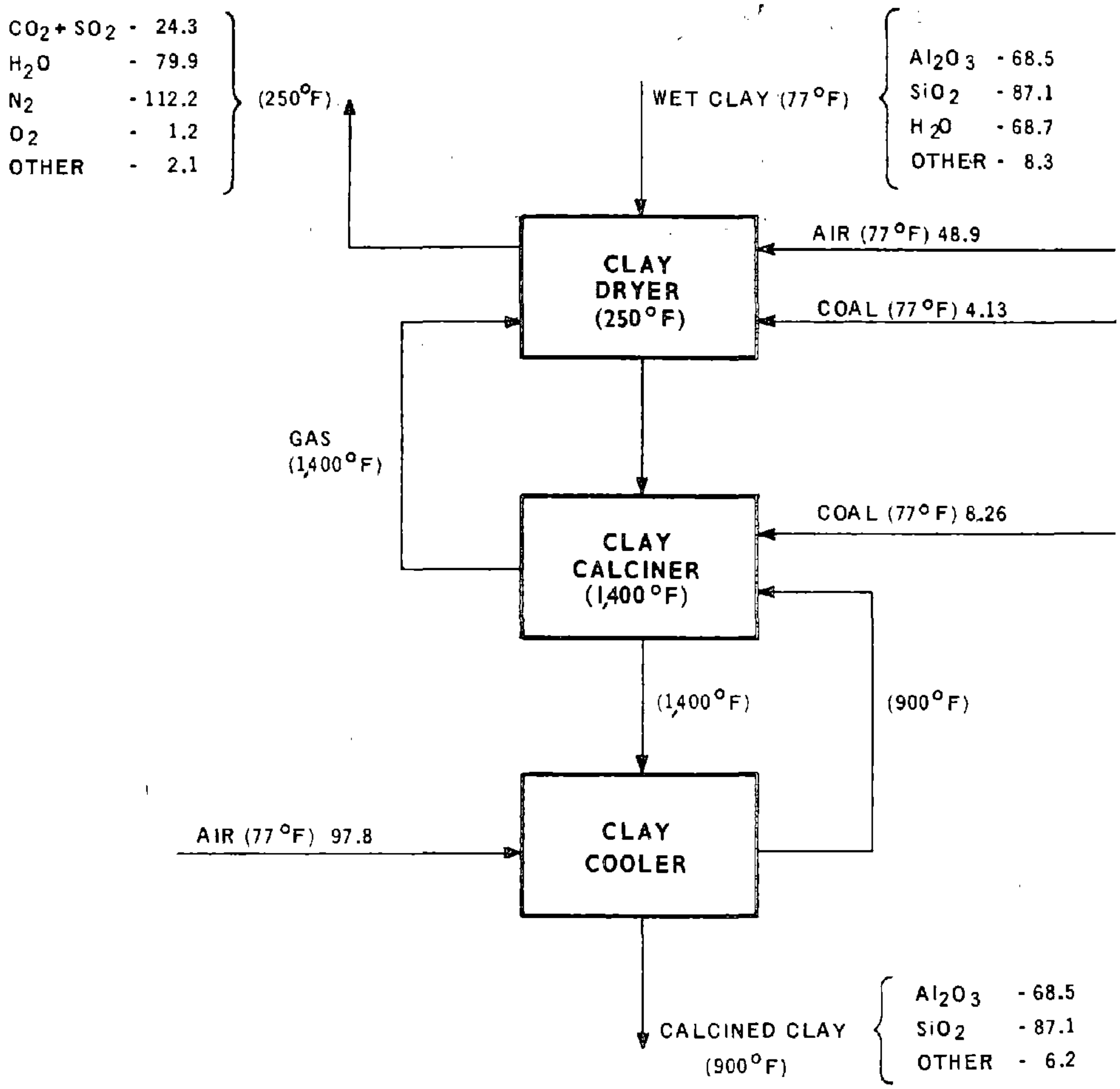
The following are heat and mass balances of three process areas:

1. Clay Drying and Calcination

2. $Al(NO_3)_3 \cdot 9H_2O$ Decomposition and Calcination

3. $AlCl_3 \cdot 6H_2O$ Decomposition and Calcination

# CLAY DRYING AND CALCINATION HEAT AND MASS BALANCE




B-2

Note: Units are in ton/h

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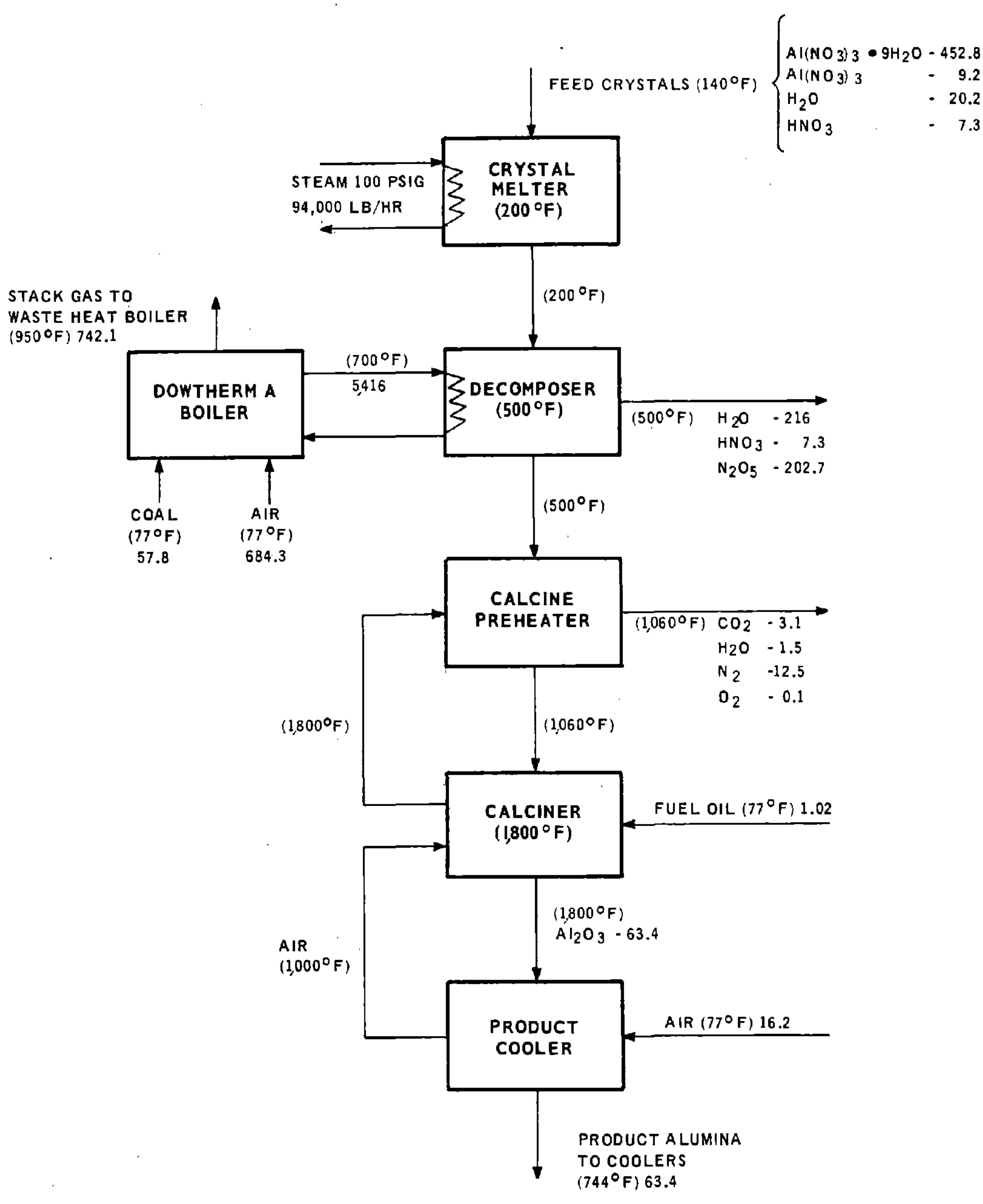
## CLAY DRYING AND CALCINATION HEAT BALANCE

| Heat Requirements | $10^6$ Btu/h |
|---|---|
| Heat of Reaction | 85.5 |
| Residual Heat in Calcined Clay | 24.0 |
| Residual Heat in Reaction Off-gas | 11.7 |
| Moisture Vaporization | 137.4 |
| Radiation Losses | 24.1 |
| Stack Loss in Coal Combustion Products | 14.8 |
| Total (Supplied by Coal) | 297.5 |

Note: Coal quality = 12,000 Btu/lb

## $AL(NO_3)_3 \bullet 9H_2O$ DECOMPOSITION AND CALCINATION HEAT AND MASS BALANCE




Note: Units are in ton/h

# $Al(NO_3)_3 \cdot 9H_2O$ DECOMPOSITION AND CALCINATION HEAT BALANCE

## Decomposition Section:

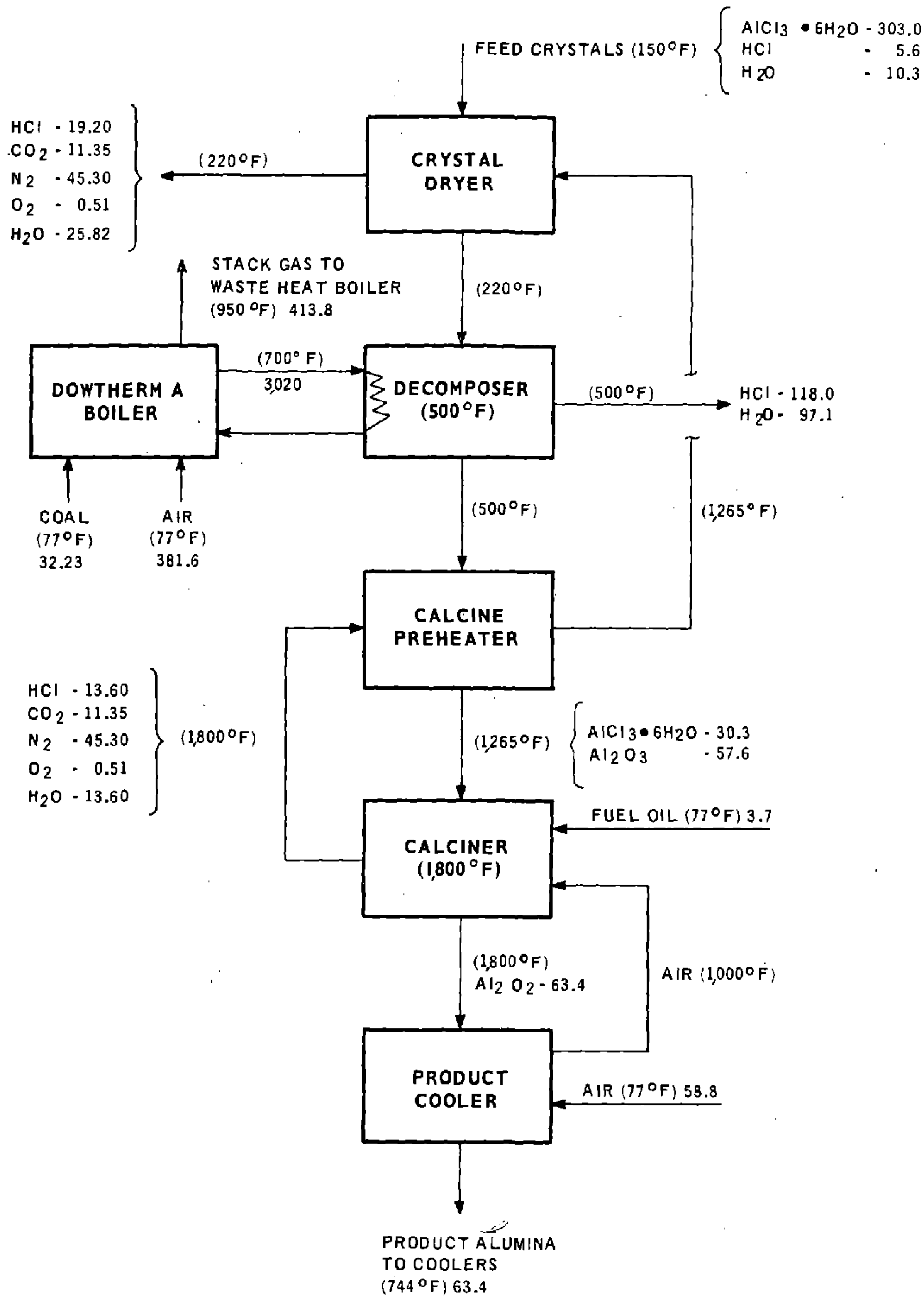
| Heat Requirements | $10^6$ Btu/h |
|---|---|
| Heat of Reaction | 755.7 |
| Residual Heat in Product | 21.8 |
| Residual Heat in Reaction Gases | 132.7 |
| Mother Liquor Vaporization | 41.3 |
| Radiation Losses | 88.9 |
| Stack Loss from Coal Combustion | 312.4 |
| Total (Supplied by Coal) | 1352.8 |

## Calcination Section:

| Heat Requirements | $10^6$ Btu/h |
|---|---|
| Residual Heat in Product | 37.0 |
| Stack Loss from Oil Combustion | 1.3 |
| Total (Supplied by Oil) | 38.3 |

Note: Coal quality = 12,000 Btu/lb
Oil quality = 18,875 Btu/lb

## $AlCl_3 \bullet 6H_2O$ DECOMPOSITION AND CALCINATION HEAT AND MASS BALANCE




Note: Units are in ton/h

# $AlCl_3 \cdot 6H_2O$ DECOMPOSITION AND CALCINATION HEAT BALANCE

## Decomposition Section:

| Heat Requirements | $10^6$ Btu/h |
|---|---|
| Heat of Reaction | 481.5 |
| Residual Heat in Product | 5.5 |
| Residual Heat in Reaction Gases | 35.2 |
| Mother Liquor Vaporization | 29.6 |
| Radiation Losses | 44.1 |
| Stack Loss from Coal Combustion | 178.8 |
| Total (Supplied by Coal) | 774.7 |

## Calcination Section:

| Heat Requirements | $10^6$ Btu/h |
|---|---|
| Heat of Reaction | 53.5 |
| Residual Heat in Product | 47.8 |
| Residual Heat in Reaction Gases | 15.9 |
| Radiation Losses | 9.4 |
| Stack Loss from Oil Combustion | 12.7 |
| Total (Supplied by Oil) | 139.3 |

Note: Coal quality = 12,000 Btu/lb
Oil quality = 18,875 Btu/lb