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Shaft Furnace Reduction-Oxidation Roasting of Pelletized Alunite Dust

By J. M. Riley, V. E. Edlund, and W. I. Nissen



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8821

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu	British thermal unit	gal/min	gallon per minute
Btu/ft ³	British thermal unit per cubic foot	g/L	gram per liter
Btu/lb	British thermal unit per pound	g-mol	gram-mole
Btu·lb ⁻¹ ·°F ⁻¹	British thermal unit per pound, per degree Fahrenheit	g/mol	gram per mole
°C	degree Celsius	h	hour
cal	calorie	hp	horsepower
cal/mole	calorie per mole	in	inch
cfm	cubic foot per minute	kg	kilogram
cm ³	cubic centimeter	kW	kilowatt
cm ³ /min	cubic centimeter per minute	lb	pound
°F	degree Fahrenheit	lb/h	pound per hour
ft	foot	L/min	liter per minute
ft ³	cubic foot	min	minute
ft ³ /h	cubic foot per hour	mL	milliliter
g	gram	mm Hg	millimeter of mercury
gal	gallon	mol	mole
gal/h	gallon per hour	pct	percent
		s	second
		vol-pct	volume-percent

SHAFT FURNACE REDUCTION-OXIDATION ROASTING OF PELLETIZED ALUNITE DUST

By J. M. Riley,¹ V. E. Edlund,² and W. I. Nissen³

ABSTRACT

The Bureau of Mines investigated a promising new technology for recovering Al_2O_3 from alunite to support the Bureau's alumina miniplant project. Results are presented for a study of the technical feasibility of treating alunite crushing and grinding reject fines for recovery of Al_2O_3 .

Alunite pellets having sufficient strength and resistance to degradation were produced by combining fines and coarse alunite with a KOH binder. The best pellets were prepared, in a laboratory pelletizer, by adding 1 pct KOH as a 5-pct solution to a mixture of 40 pct alunite dust (98 pct minus 65 mesh) and 60 pct coarse alunite (minus 20 plus 65 mesh).

Calcines suitable for K_2SO_4 and Al_2O_3 recovery were produced by reducing dehydrated alunite pellets with sulfur in a laboratory shaft furnace for 4 h at 600°C , followed by air oxidation of the reduced calcine for 1 h at 600°C . This report presents design calculations, schematic diagrams, and discussions of the essential features of a proposed process research unit (PRU)--a continuous, 6-lb/h alunite shaft furnace--for studying the process.

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INTRODUCTION

The Bureau of Mines, as part of its mission to encourage the use of domestic resources to meet at least part of the Nation's requirements for critical and strategic minerals, investigated technology options for extracting alumina (Al_2O_3) from domestic nonbauxitic resources. Bauxite, an ore containing about 50 pct Al_2O_3 , is the traditional alumina source. The United States has minimal resources of bauxite; net imports of bauxite and alumina account for more than 93 pct of the aluminum raw materials used in the United States. Because of this import reliance, the Bureau initiated a research program based on a raw material-process technology matrix that considered domestic nonbauxitic resources and promising technologies for extracting Al_2O_3 from them. Resources considered were clay, anorthosite, alunite, dawsonite contained in oil shale, and coal ash and coal shale. The most promising raw material-process technology options were scheduled for investigation in a miniplant at the Bureau's Boulder City (Nev.) Engineering Laboratory. Projects were begun in other Bureau research centers to solve problems that arose in connection with the miniplant research or that were known to exist in the technology options being considered for miniplant studies.

Alunite [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$] has been recognized as a potential source of Al_2O_3 for many years (2),⁴ and the U.S.S.R. is known to have made Al_2O_3 from its alunite deposits for smelting into aluminum. With the discovery in 1970 of new, large alunite deposits in the Wah Wah Mountains, about 50 miles northwest of Cedar City, UT, interest in this material quickened. These deposits, reported at over 100 million tons of ore, contain 14 pct Al_2O_3 (5).

A pilot plant was built and operated by the Alumet Co., a consortium of private companies, to recover Al_2O_3 , K_2SO_4 , and H_2SO_4 from Utah alunite. The company reportedly used purchased Soviet technology in its development work. The roasting process consists of (1) dehydration of alunite to remove chemically combined water, (2) sulfur reduction of alunite to reduce the $\text{Al}_2(\text{SO}_4)_3$ component to Al_2O_3 and SO_2 , and (3) oxidation of calcine to oxidize any sulfides produced during reduction (4). The SO_2 evolved is converted to H_2SO_4 . The K_2SO_4 is water-leached from the calcine, leaving inert quartz and activated Al_2O_3 , which is recovered by a modified Bayer process.

A critical step of the process is the reduction operation. Improved techniques are especially needed for efficient reduction of the minus 200-mesh fraction of the ground ore, without prohibitive dust losses. If minus 20-mesh Utah ore is fed directly to a fluidized-bed roaster, 10 pct or more of the Al_2O_3 content of the ore could be lost in the dust fraction. The objectives of this investigation were to identify the variables and process conditions that should be tested, to develop design data for a process research unit (PRU), and to prepare a proposal for a PRU.

This report presents the results of an investigation made to explore the merits of treating pelletized alunite fines, using shaft furnace techniques. The first part of the report deals with laboratory investigations on pelletizing, reduction-oxidation roasting in electrically heated 2- and 3-in-diam shaft furnaces, and leaching of roasted calcines. The second part of the report presents a design proposal for a PRU to study reduction-oxidation of alunite pellets under dynamic conditions.

⁴Underlined numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.

RAW MATERIALS

Two samples of alunite ore provided by the Alumet Co. were used in the investigation--dust product from the dust collection system of the pilot-plant grinding circuit and minus 8-mesh ore from the crushing circuit. The coarse material was further ground to minus 20 mesh to approximate Alumet's feed to the fluidized-bed roaster. A screen analysis of the dust and minus 20-mesh material (table 1) showed the dust to be essentially finer than 200 mesh; 43 pct of the minus 20-mesh ore sample was finer than 200 mesh.

TABLE 1. - Screen analysis of alunite samples, weight percent

Mesh size	Ore	Dust
Minus 20 plus 35.....	19.4	0.25
Minus 35 plus 48.....	11.4	.55
Minus 48 plus 65.....	8.4	.95
Minus 65 plus 100.....	6.7	1.95
Minus 100 plus 200.....	11.0	9.6
Minus 200.....	43.1	86.7

Chemical analyses of the two samples (table 2) revealed the dust to be richer in Al_2O_3 than the ore. Softer alunite grinds more readily than opal-quartz

gangue (5) and tends to concentrate in the fines.

TABLE 2. - Chemical analyses of alunite samples, weight percent

Component	Ore	Dust
Al.....	9.5	11.6
K.....	3.9	4.5
SO ₄	21.2	24.0
SiO ₂	52.8	41.0
Fe.....	.7	.7
Na.....	ND	.22

ND Not determined.

Sulfur beads, used in reduction-roast tests, were formed by pouring liquid sulfur into a stirred column of cold water. Sulfur beads were screened to obtain a minus 6- plus 10-mesh fraction, a convenient size for feeding to the laboratory furnace.

The Ar, CO₂, CO, N₂, and O₂ gases used in the roasting tests were commercially available compressed gases. Pellet binders--KOH, K₂SO₄, bentonite, molasses, and calcium lignin sulfonate--were commercially available chemicals or products.

TEST PROCEDURES AND EQUIPMENT

The general test procedure comprised (1) pelletizing selected mixtures of dust and crushed ore, (2) heating the agglomerated mix at 600° C (proposed by Alumet (5)) in a muffle furnace to remove chemically combined water, and (3) reduction-oxidation roasting the dehydrated pellets in a vertical tube furnace simulating shaft furnace conditions. During the test procedure, oxidized calcines were cooled in a stream of inert gas, to prevent oxidation of excess S₈ and SO₂ and sulfation of Al₂O₃. Calcine was subsequently removed from the furnace and weighed. After being weighed, representative portions of each calcine were pulverized and water-caustic-leached for process evaluation, and the products were analyzed for total S₈, S⁻², SO₄⁻², K, Fe, Al, and SiO₂. Mass balances were computed from the test data.

PELLETIZING

Weighed portions of dust and crushed ore were mixed dry, and the mixture was pelletized in an 18-in-diam stainless steel drum pelletizer, shown in figure 1. Usually, 1 kg of dry charge was fed slowly to the pelletizer while the moving bed was simultaneously sprayed with about 200 mL of binding solution. At periodic intervals, the bed was screened to separate minus 1/2- plus 1/4-in pellet product.

Green pellets were dried for 16 h or more at 110° C and tested for strength by being pressed between a steel plate and a spring-type platform scale. The force required to fracture a 3/8-in-diam pellet was designated pellet strength. Calcined pellet degradation was evaluated by screening the calcine on a



FIGURE 1. - Laboratory disk pelletizer.

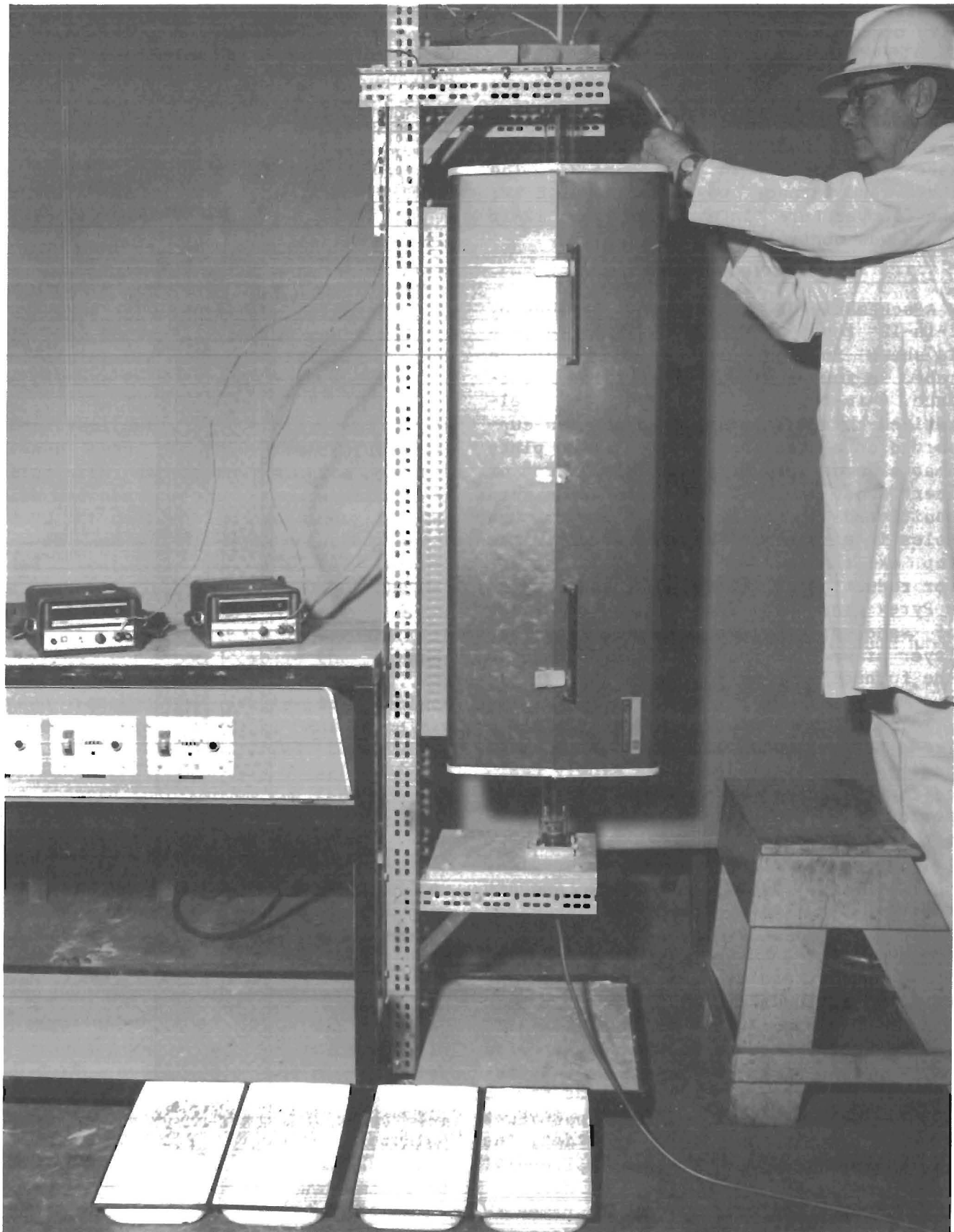


FIGURE 2. - Laboratory shaft furnace.

65-mesh screen and determining the quantity of minus 65-mesh material.

ROASTING

Reduction-oxidation tests were performed in a vertically mounted tube furnace assembly, shown in figure 2. The three-zone furnace was rated at 6.8 kW; the temperature in each of the 12-in zones was controlled automatically.

BATCH TESTS

A schematic drawing of the 5-ft-long by 2-in-ID fused quartz shaft furnace tube is shown in figure 3. In this furnace tube, a four-zone bed comprising alternate 4-in-thick, 200-g layers of pelletized charge and Berl⁵ saddles was supported on a stainless steel orifice plate that allowed for entry and dispersion of inert sweep gas. Thermocouple wells were positioned in the reaction zone through holes in a rubber stopper mounted in the top of the furnace tube. Sulfur beads for reduction of alunite were fed through a Pyrex glass tube into the bottom layer of saddles. Sulfur vaporized in this layer of saddles and was diffused through the furnace tube by the sweep gas.

To minimize the possibility of localized hotspots that would cause alumina passivation, the furnace was slowly heated to the desired temperature over a 5-h period. During heating, a stream of inert gas was passed through the charge to displace air, complete dehydration, and circulate heat. After the furnace reached the test temperature, 1.25-g charges of sulfur beads were dropped into the sulfur feed tube at 10-min intervals. This sulfur feed rate, equivalent to one stoichiometric weight of sulfur per hour per zone, was held constant for all tests. The sweep gas flow was controlled at 0.4 L/min, resulting in a gas contact time of 6 s and a reducing gas stream containing 10 vol-pct S₂ vapor. In some tests, following reduction roasting, the furnace charge was oxidized in air and/or

oxygen for 1 h at 600° C. After roasting, sulfur feed was discontinued, power to the electric furnace was switched off, and the charge was allowed to cool in a stream of inert gas for 16 h.

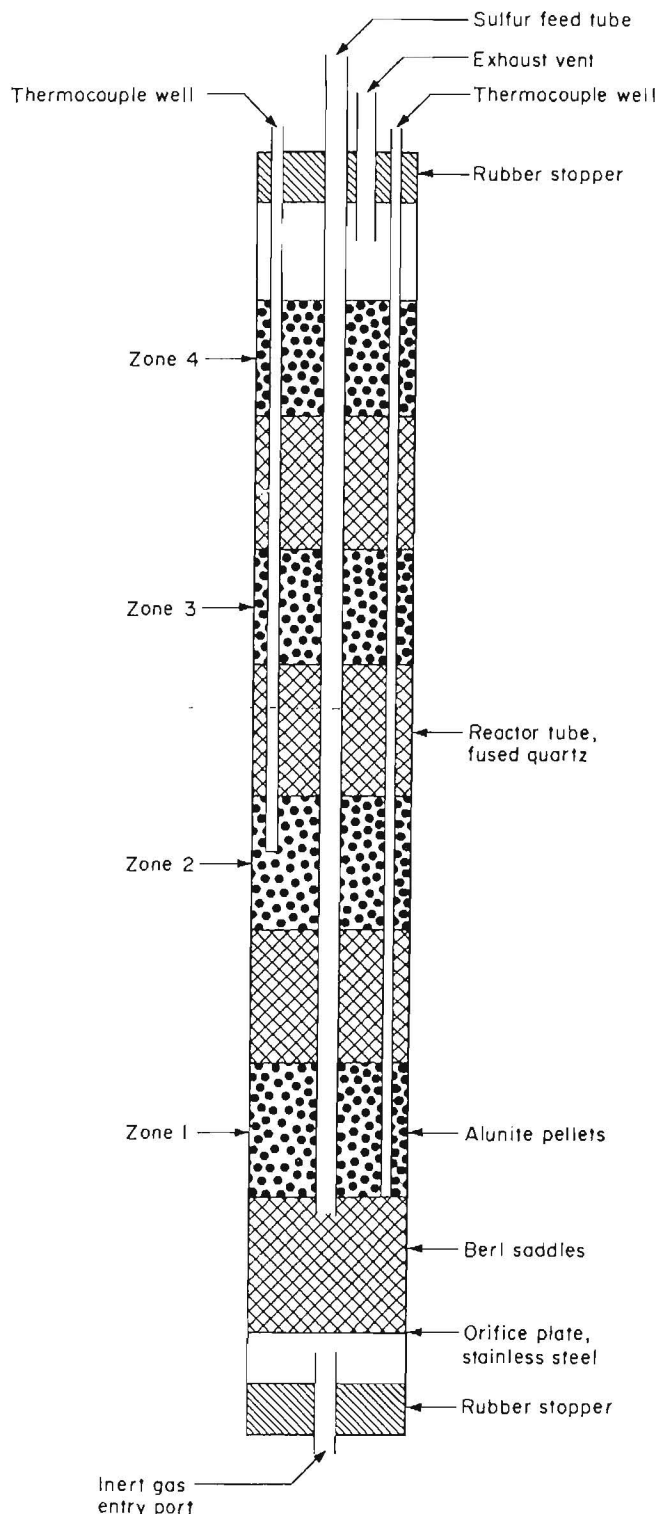


FIGURE 3. - Schematic drawing of loaded shaft furnace tube for batch tests.

⁵Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

SEMICONTINUOUS TESTS

A schematic drawing of the 5-ft-long by 3-in-ID fused quartz shaft furnace tube is shown in figure 4. A movable firebrick hearth was installed underneath the furnace tube. Sweep gas tuyeres were installed through the hearth into the furnace tube. Thermocouple wells were positioned in the reaction zone through holes in a rubber stopper mounted in the top of the furnace tube. Sulfur beads for alunite reduction were fed through a Pyrex tube into the bed of calcine, 3 in above the tuyeres. Sulfur vaporized in the calcine bed and was dispersed through the furnace tube by sweep gas.

For semicontinuous tests, the shaft furnace tube at room temperature was filled with dehydrated alunite pellets, which had been prepared from alunite that was 90 pct dust and 10 pct minus 20 plus 65 mesh and a 5-pct-KOH solution, which added about 1 pct to the feed weight. The loaded furnace was heated to the desired temperature for 5 h to reduce the chance of Al_2O_3 passivation occurring in localized hotspots. While the furnace was heating, a stream of nitrogen was passed through the charge to displace air, complete dehydration, and circulate heat. After the $600^\circ C$ test temperature was reached, 11-g charges of sulfur beads were dropped into the sulfur feed tube at 30-min intervals. Nitrogen sweep gas flow was adjusted to 1.37 L/min to give a reactant gas containing 7 vol-pct S_2 . At 2-h intervals, 660 g of calcine were removed from the hearth and the shaft furnace was refilled. Calcines produced under these conditions were not oxidized.

WATER-CAUSTIC LEACHING

A standard water-caustic leach, developed during operation of the Alumet pilot plant, was employed for evaluating calcines. The water leach (for reduction-oxidation products) entailed leaching samples of minus 65-mesh calcine for 30 min at $90^\circ C$. Water was added as

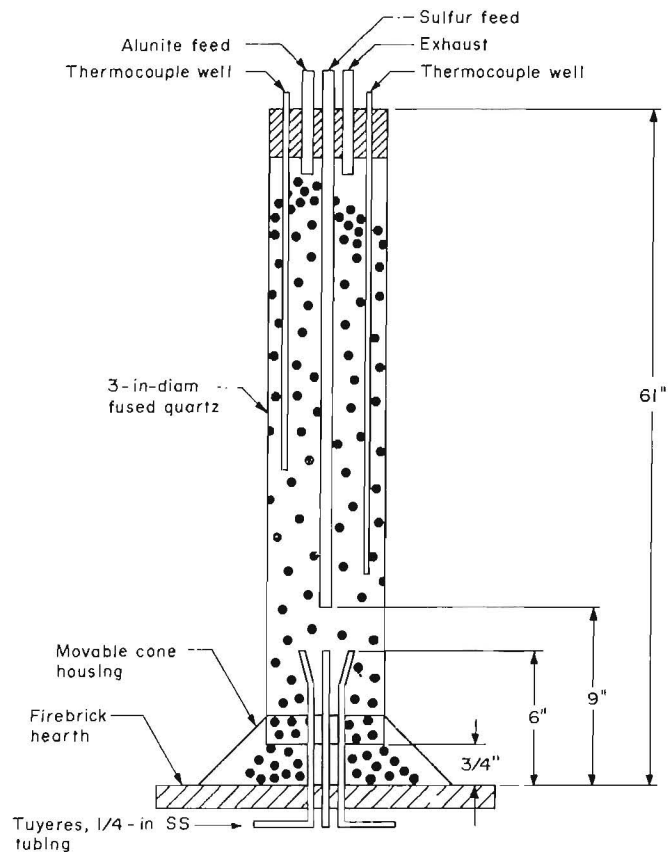


FIGURE 4. Schematic drawing of shaft furnace tube for semicontinuous tests.

necessary to maintain the pulp at 35 pct solids. The slurry was filtered and the filter cake washed four times with hot water. The washed solids were dried and submitted for chemical analysis with the combined filtrate and washes.

A caustic leach (modified Bayer process evaluation) of the water-leach residue was made for 30 min at $90^\circ C$ using a 190-g/L NaOH leach solution and adding water as necessary to maintain leach pulp at 26 pct solids. The slurry was filtered and the solids were washed five times by displacement with hot wash solution. Wash solution was prepared by dissolving 1 g NaOH in a liter of water. Both water and caustic leaches were made in 400-mL stainless steel beakers to minimize dissolution and contamination of the product leach liquor with SiO_2 .

TEST RESULTS

PELLETIZING

The pelletizing studies established conditions for agglomerating alunite fines to produce a feed suitable for a process using shaft furnace roasting techniques. Two factors that principally influenced the formation of satisfactory pellets were (1) ratio of coarse-to-fine particles and (2) pellet binder. The results of pelletizing tests showing the effect of different particle size distributions and pelletizing binders are presented in table 3. These tests showed pellet strength can be increased by using a KOH binder and controlling size distribution of alunite in the pellet mix. Potassium hydroxide may be produced by causticizing the K_2SO_4 product produced in Alumet's process. Addition of coarse alunite sizes improves both crushing strength and degradation resistance. However, pellets prepared by adding 1 pct KOH as a 5-pct-KOH solution to minus

200-mesh (dust) alunite may be strong enough for handling and roasting.

ROASTING

Preliminary studies

Preliminary reduction tests of pelletized alunite fines in a laboratory shaft furnace were run at 600° C for 2 h. These tests, using 1,000 cm³/min of 20 pct CO-Ar or 20 pct S₂-Ar gas mixtures, showed sulfur elimination of over 90 pct for both reductants. However, chemical analysis showed the percentage of FeS and K₂S to be almost five times greater in the CO-reduced calcine. This indicated an inefficient use of CO as the result of overreduction of alunite and the need for oxidation of the CO-reduced calcine. Emphasis was placed, therefore, on determining conditions for sulfur reduction of alunite because sulfur is considered a milder reductant than CO.

TABLE 3. - Effect of binders and size distribution on alunite pellet strength and resistance to degradation

Alunite particle size, mesh	Binder		Dry pellet strength, lb	Calcined pellet strength, lb	Calcined pellet degradation, minus 65 mesh, pct
	Type	Pct of feed			
Minus 20 plus 65 (60 pct), minus 200 (40 pct).	5-pct KOH.....	1	10	5	0.35
Minus 20 plus 65 (30 pct), minus 200 (70 pct).	...do.....	1	6	ND	ND
Minus 20 plus 65 (10 pct), minus 200 (90 pct).	...do.....	1	5	ND	ND
Minus 65.....	...do.....	1	7	5	3.5
Minus 200.....	...do.....	1	5	3	3.5
Do.....	Water.....	0	1	1	ND
Do.....	Bentonite.....	3	1.5	ND	ND
Do.....	Molasses.....	3	1	ND	ND
Do.....	Calcium lignin sulfonate.	5	1	ND	ND
Do.....	Saturated K ₂ SO ₄	ND	1	ND	ND

ND Not determined.

In other tests, it was determined that during reduction essentially all the iron in the ore is converted to FeS. There are some data suggesting that sulfide sulfur inhibits solubility of potassium. Alumet (5) proposes in its process to re-oxidize the sulfides in the reduced calcine to yield a product suitable for K_2SO_4 and Al_2O_3 leaching.

Batch Sulfur Reduction-Oxidation

Temperature Studies

Reduction tests of pelletized alunite dust were conducted at 550°, 600°, and 650° C for 4 h. The data in table 4 for the calcine from zone 1 show the percentage of sulfur eliminated from the $Al_2(SO_4)_3$ component and the water-soluble potassium. These results show that the best sulfur elimination and potassium extraction were obtained at a roasting temperature of 600° C.

TABLE 4. - Effect of reduction temperature on sulfur elimination and potassium extraction in zone 1, 4-h roast

Temp., °C	S elimination, ¹ pct	K extraction, pct
550.....	57	63
600.....	87	90
650.....	96	74

¹ $Al_2(SO_4)_3$ sulfur.

Time Studies

Reduction tests of pelletized alunite dust were conducted for 3, 4, and 5-1/2 h at 600° C, and also for 1-1/2 and 4 h at 650° C. Table 5 shows the percentage of sulfur elimination from $Al_2(SO_4)_3$ in alunite and potassium extraction from the calcine in the standard water leach for furnace zone 1. These results show that additional studies must be completed to determine the optimum roasting time.

TABLE 5. - Effect of reduction time on sulfur elimination and potassium extraction in zone 1

Time, h	Temp., °C	S elimination, ¹ pct	K extraction, pct
3.....	600	84	86
4.....	600	87	90
5-1/2.	600	86	86
1-1/2.	650	68	73
4.....	650	96	74

¹ $Al_2(SO_4)_3$ sulfur.

Furnace Profiles

Samples of calcine from each of the four zones were analyzed chemically to determine sulfur elimination and water-leached to determine the extraction of potassium. Table 6 shows results obtained in reduction roasting and reduction-oxidation roasting for a 4-h reduction time at 600° C. The calcine analyses for sulfide and sulfate show that the reducing roast produces sulfide compounds and the oxidizing roast converts the sulfide to sulfate. The effect of sulfide on the extraction and recovery of K_2SO_4 and Al_2O_3 needs to be investigated further.

TABLE 6. - Shaft furnace profiles at 600° C

Calcine analysis, pct	Zone 1	Zone 2	Zone 3	Zone 4
Reduced:				
S ⁻²	0.7	0.4	0.4	0.1
SO ⁻²	8	8	8	20
S ₄ elimination ¹	87	89	91	29
K extraction.....	90	91	89	37
Reduced and oxidized:				
S ⁻²	<.1	<.1	<.1	<.1
SO ⁻²	11	10	11	24
S ₄ elimination ¹	84	84	79	11
K extraction.....	84	85	84	23

¹ $Al_2(SO_4)_3$ sulfur.

KOH Pellet Binder Studies

Typical roasting results for furnace zone 1, showing the effect of KOH pellet binders, are presented in table 7. Pelletized alunite dust was reduced for 4 h at 600° C. These results suggest that the KOH pellet binder reduces porosity and inhibits reduction of alunite.

TABLE 7. - Effect of KOH pellet binder on 600° C roasting of pelletized alunite dust

Pellet binder	S elimination, ¹ pct	K extraction. pct
Water.....	87	90
KOH.....	73	76

¹Al₂(SO₄)₃ sulfur.

Pellet Particle Distribution Studies

Table 8 shows furnace zone 1 results of roasting pellets prepared with KOH and feeds having various particle size distributions. Pellets were reduced for 4 h at 600° C. These results show that use of a coarser size distribution facilitates reduction of the pellets.

TABLE 8. - Effect of pellet particle size distribution on roasting

Screen size, Tyler mesh	S elimination, ¹ pct	K extraction, pct
Minus 200.....	73	76
Minus 65.....	87	90
Minus 20.....	94	81

¹Al₂(SO₄)₃ sulfur.

Furnace Gases

Sweep gases for the roasting tests include Ar, N₂, or N₂-CO₂. Results shown in table 9 indicate that these gases did not affect roasting. During reduction and oxidation the furnace offgas contained SO₂. Condensed sulfur was not observed on the cool exhaust-vent tube. The concentration of SO₂ evolved ranged from 20 to 80 pct.

TABLE 9. - Effect of sweep gas composition on roasting

Sweep gas constituents	S elimination, ¹ pct	K extraction, pct
Ar.....	86	86
N ₂	84	91
N ₂ -CO ₂	87	90

¹Al₂(SO₄)₃ sulfur.

Semicontinuous Sulfur Reduction

The results for a semicontinuous operation (table 10) show that roasting alunite for 4 h at 600° C is adequate for maximum recovery of K₂SO₄ and Al₂O₃. Other semicontinuous test results suggest a need to investigate more fully reduction and passivation at lower and higher temperatures. The results show calcines are passivated with a 650° C roast temperature and a roasting time greater than 4 h.

TABLE 10. - Semicontinuous shaft furnace reduction of alunite with 7 pct S₂ vapor at 600° C

Calcine retention time, h	S elimination, ¹ pct	Solubility	
		Water leach: K, pct	Caustic leach: Al, pct
2.....	64	84.5	63.2
4.....	86	91.0	85.8
6.....	90	90.1	80.7
8.....	81	90.0	81.0

¹Al₂(SO₄)₃ sulfur.

WATER-CAUSTIC-LEACH EVALUATION OF CALCINE

A typical standard water leach residue contained, in percent, 25.1 Al₂O₃, 0.6 K, 1.8 SO₄, 47.4 SiO₂, and 0.8 Fe. Standard caustic leach of this residue extracted 90 pct of the aluminum in an impure solution containing, in grams per liter, 0.06 P, 0.07 SiO₂, 0.005 V, and 20 Al₂O₃.

DESIGN PROPOSAL FOR CONTINUOUS PRU SHAFT FURNACE

Batch roasting studies showed the technical feasibility of achieving sulfur reduction of pelletized alunite fines in a shaft-type furnace. The next phase of the investigation should entail a study of the reduction step on a larger scale under continuous operating conditions. The PRU shaft furnace would employ internal heating and a continuously moving bed of pellets, as opposed to external heating and the static bed employed in batch studies.

The PRU furnace operation should be evaluated to determine the effects of direct heating, to understand the influence of reduction time and temperature on passivation of Al_2O_3 , and to measure sulfur reduction efficiency. Samples of the reduction roast product would be oxidized and water-leached; water-leach residues would be leached with caustic to determine Al_2O_3 extraction.

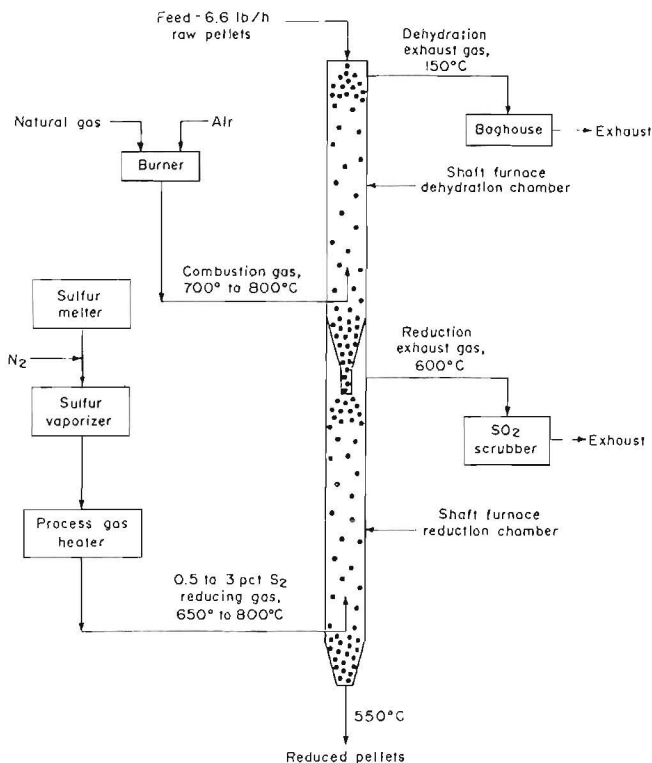


FIGURE 5. Flow diagram of a proposed PRU assembly for the sulfur reduction of pelletized alunite fines.

A flow diagram for a proposed PRU assembly is shown in figure 5. Essential features of the test unit include (1) a vertical furnace chamber for carrying out dehydration and reduction, (2) a sulfur melter and vaporizer, (3) a burner for generating dehydration heat, (4) an electric process gas heater, (5) an SO₂ gas scrubber, and (6) a baghouse. Auxiliary equipment would include (1) a gas chromatograph, (2) a multipoint temperature recorder, (3) gas flowmeters, (4) bottled nitrogen, and (5) exhaust fans.

OPERATING CONDITIONS

Initial operation of the PRU furnace (see figures 5 and 6) assumes a feed rate of 6.6 lb/h of partially dried green pellets (6.0 lb dry basis), 0.25 lb/h of elemental sulfur, a 4-h reaction time, and a 6-in-diam dehydration-reduction

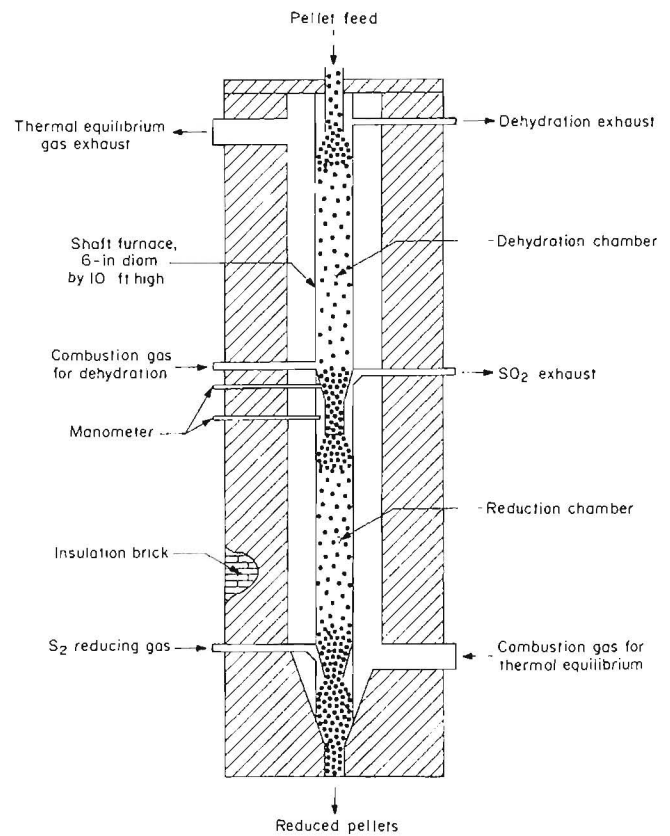


FIGURE 6. Cross-sectional drawing of PRU shaft furnace

chamber. Selection of a 6-in reaction chamber was based on pellet flow considerations and to minimize channeling of reaction gases and bridging of pellet feed.

The sulfur feed rate of 0.25 lb/h is 144 pct of the theoretical amount required to react with the $\text{Al}_2(\text{SO}_4)_3$ component of alunite. An excess of sulfur is required to ensure complete reduction of the $\text{Al}_2(\text{SO}_4)_3$ and to provide the sulfur to form sulfides with the small amount of iron in the ore.

Partially dried raw pellets are charged cold through the top of the furnace. Process heat for the dehydration chamber is supplied by natural gas burned in a direct-fired heater. Combustion gases tempered to 800° C with secondary air enter through the bottom of the dehydration chamber, rise countercurrent to the flow of pellets, and discharge to the atmosphere at 150° C. After removal of free and dehydrated water, hot 650° C pellets discharge directly into the reduction chamber.

Sulfur vapor, mixed with carrier gas preheated in an electric tube furnace, is fed into the reduction zone at 650° C or higher. Gaseous reaction products discharge from the reduction zone at 600° C; reduced pellets discharge at 550° C. Under these conditions, sensible heat available in the carrier gas can supply approximately 55 pct of the heat required to sustain endothermic reduction reaction. The remaining 45 pct is furnished by heat transferred to the gas streams as the pellets cool from 650° C to 550° C.

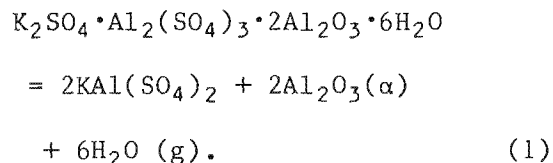
Additional details on anticipated operating conditions are presented in appendix A.

HEAT REQUIREMENTS

Heating requirements for dehydration and reduction zones differ. The following sections discuss individual requirements for each of these operations.

Dehydration

The reaction for dehydration of alunite is given by the following expressions (3):



$$\Delta H_T^\circ = 149,530 - 5.3 T, \quad (2)$$

where T is the temperature in kelvins.

In addition to energy required for dehydration, combustion heat must also be supplied to the dehydration chamber to (1) remove free water in the raw pellets and exhaust moisture to the atmosphere at 150° C and (2) raise pellet temperature to 650° C. A portion of the sensible heat associated with dehydration water vapor would be recovered by countercurrent heat transfer occurring when the vapor stream from the 650° C dehydration zone cools to the 150° C exhaust temperature. Heat requirements for different operations carried out in the dehydration chamber are presented in table 11.

TABLE 11. - Heat required for dehydration

<u>Operation</u>	<u>Btu/6.6 lb alunite pellets, wet</u>
Heat required to eliminate free water.....	691
Heat required to raise temperature of dry pellets to 650° C.....	1,782
Heat required to dehydrate dry alunite pellets	944
Heat recovered from dehydration water vapor in cooling from 650° to 150° C.....	-179
Total theoretical heat required to dehydrate 6.6 lb ore.....	3,238

TABLE 12. - Heat available and required for reduction

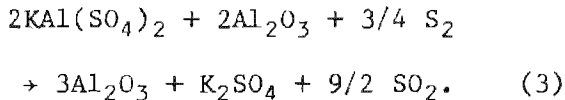
	<u>Btu/6.0 lb alunite pellets, dehydrated</u>
Sensible heat from cooling dehydrated pellets from 650° to 550° C.....	263
Heat supplied by nitrogen carrier gas.....	<u>313</u>
Total theoretical heat required to reduce 2.61 lb dehydrated alunite contained in 6.0 lb dry pellets	576

The theoretical value of 3,238 Btu represents the net heat requirement. Since combined thermal efficiency of the combustion gas heater plus the dehydration operation is 74.7 pct (see appendix B), the gross heat requirement would increase to 4,335 Btu. This would be furnished by 4.33 ft³ of natural gas burned in a direct-fired heater operation at an estimated thermal efficiency of 90 pct. A combustion value of 1,000 Btu/ft³ (net) is assumed for natural gas. Combustion gas, cooled with secondary air to 800° C, would be fed into the bottom of the dehydration chamber.

Additional heat balance information on the dehydration step is presented in appendix B.

Reduction

Sulfur reduction of dehydrated alunite may be expressed by the following reaction:



The reduction reaction is endothermic. At 600° C, the proposed reduction temperature, H₈₇₃^o = 88,164 cal (350 Btu), and a theoretical heat input of 145,043 cal (576 Btu) to the reduction chamber would be required to reduce 2.61 lb of dehydrated alunite contained in 6.6 lb of raw alunite ore pellets.

Process heat for reduction would be supplied by (1) a 100° C pellet temperature drop through the reduction chamber and (2) sensible heat in the nitrogen carrier gas. The quantity of carrier gas

required would depend upon the temperature of the reduction gas stream. A carrier gas input temperature range of 650° to 800° C is assumed for initial operation of the PRU furnace.

Heat values supplied by the respective sources are presented in table 12. A heat capacity value of 0.26 Btu·lb⁻¹·°F⁻¹ is assumed for dehydrated pellets and 0.25 Btu·lb⁻¹·°F⁻¹ for nitrogen. Additional heat balance information on the reduction step is presented in appendix C.

EQUIPMENT DESCRIPTION

The overall PRU system includes the following components:

1. Shaft furnace unit.
2. Sulfur vaporizer.
3. SO₂ gas scrubber.
4. Baghouse.

The following sections present the basic design concept for each of these components.

Shaft Furnace Unit

Figure 6 shows a diagram of the shaft furnace for the proposed PRU assembly. The furnace shaft consists of a 6-in-diam stainless steel cylindrical chamber approximately 10 ft high. The dehydration chamber is separated from the reduction chamber by a cone section having a smaller diameter throat. Manometers positioned above and below the throat

monitor gas pressure, adjusted to minimize mixing of the dehydration and reduction gas products. Temperature control is maintained by thermocouples in the pellet bed. Quartz viewports mounted in the furnace shaft wall allow visual observation of pellets in the reaction chamber.

The dehydration-reduction furnace chamber is enclosed in a 42-in-diam steel shell lined with 12 in of refractory brick. This arrangement allows for a 5-in annular space surrounding the furnace shaft. A flow of hot combustion gas through this space maintains thermal equilibrium, resulting in essentially no loss of heat through the walls of the dehydration-reduction chambers. Natural gas burned in a direct-fired heater supplies combustion gas.

Sulfur Vaporizer

The sulfur vaporizing system (fig. 7) consists of (1) a steam-heated 1-gal autoclave, (2) a 2-kW tube furnace, (3) six standard nitrogen tanks with manifold, pressure gages, and flowmeter, (4) a 2-gal vessel for silicone fluid, and (5) a positive displacement pump to meter 0.015 gal/h of silicone fluid.

Lump sulfur is loaded manually each day into the autoclave. After the sulfur is melted and heated to 300° F, the upper section of the autoclave is filled with silicone fluid and pressurized with the metering pump. As silicone fluid is pumped into the autoclave, an equivalent volume of molten sulfur flows into the hot zone of the tube furnace and vaporizes. Nitrogen feeds into the tube

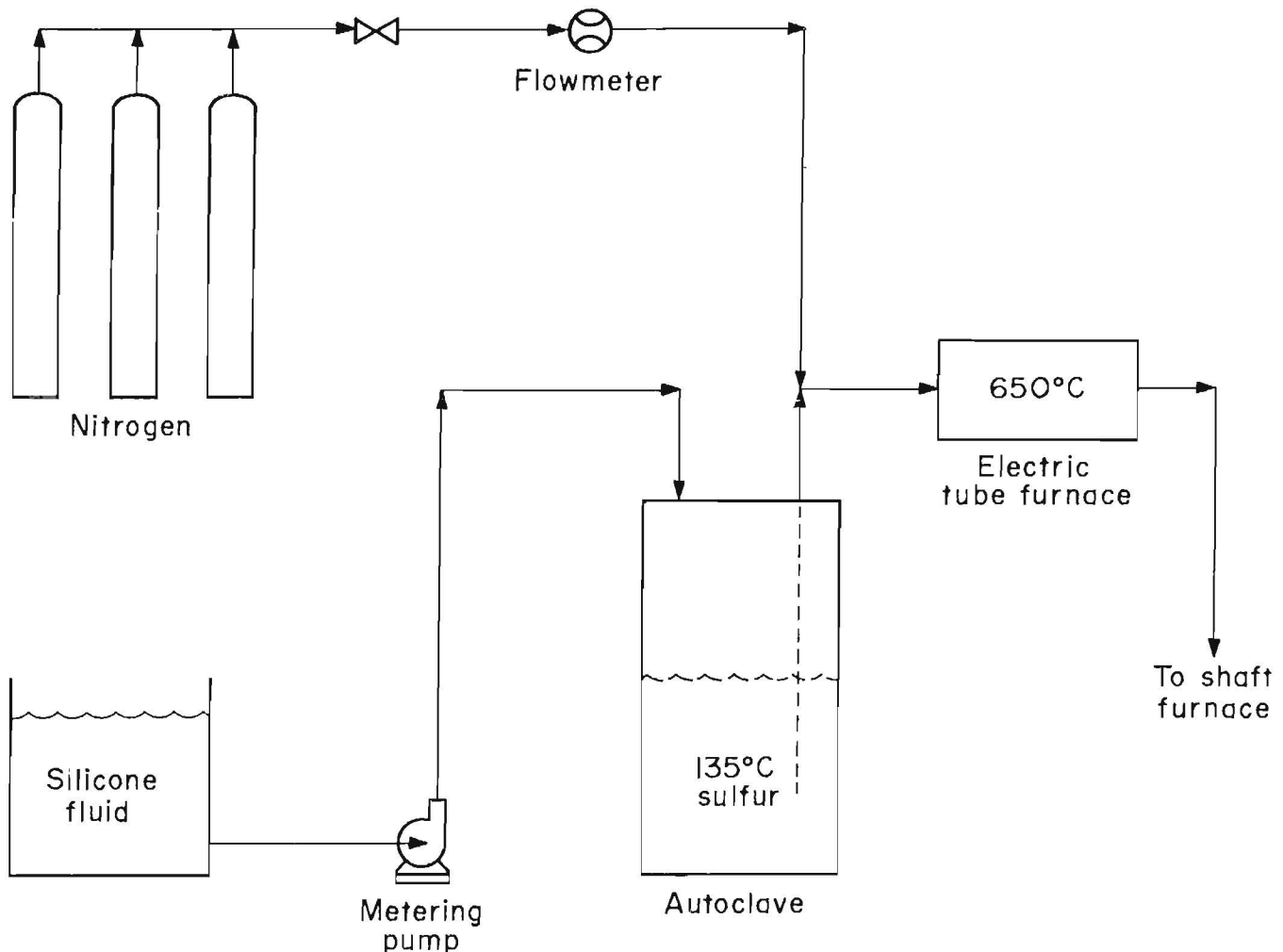


FIGURE 7. - Schematic drawing of sulfur vaporizer.

furnace, mixes with sulfur vapor, and passes on into the reducing chamber of the shaft furnace.

SO₂ Gas Scrubber

A soda ash scrubbing system is used to absorb SO₂ generated during reduction. Based on flue gas desulfurization practice, an 0.4N soda ash solution will be used to absorb SO₂. A schematic of the system is shown in figure 8. The gas scrubber unit consists of a vessel 2 ft in diameter and 8 ft high, containing 4 ft of 1-in plastic saddles supported 2 ft from the bottom. A 1-gal/min centrifugal pump circulates soda ash solution from the holding tank to the top of the scrubber. A 1-hp blower draws gas from the shaft furnace reduction stage into the bottom of the packed tower and then forces SO₂-free exhaust into a stack. Periodically, solution loaded with Na₂SO₃ (sodium sulfite) is discharged to waste and replaced with fresh 0.4N soda ash solution. Low-level SO₂ exhaust gas is discharged from the top of the scrubber.

Baghouse

Dust from the drying and dehydration stage of the shaft furnace is captured in a small laboratory baghouse. A suitable unit is the Torit model 64, which has twenty-two 24-in-long by 8-in-diam bags

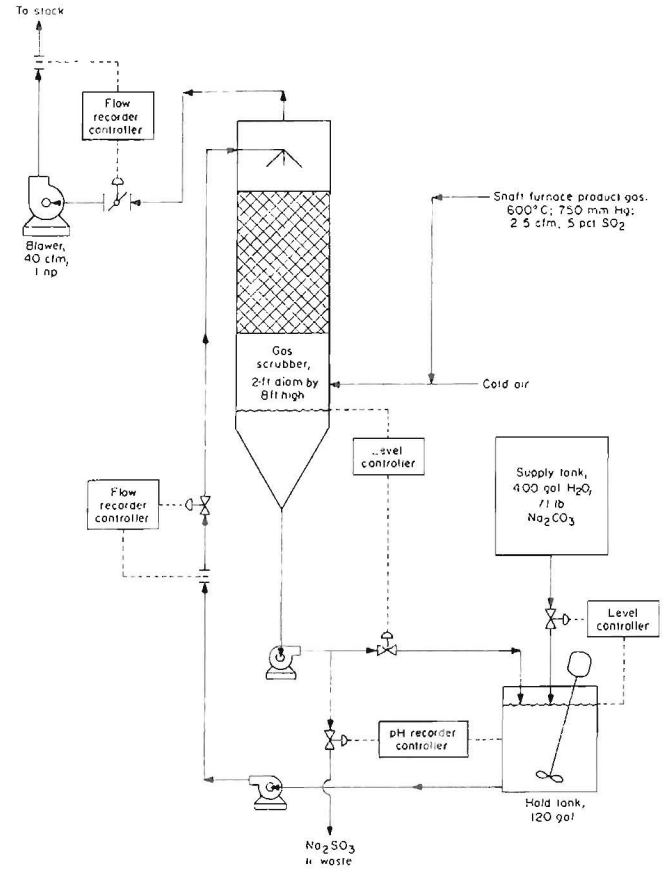


FIGURE 8. - SO₂ gas scrubber PRU flow diagram

and a 1/2-hp blower. Fiberglass bags should be used to withstand 149° C exhaust temperatures and occasional blasts of 427° C.

CONCLUSIONS AND RECOMMENDATIONS

Calcines suitable for K₂SO₄ and Al₂O₃ recovery may be produced by reducing alunite pellets with sulfur in a shaft furnace for 4 h at 600° C, followed by oxidation of the reduced calcine for 1 h at 600° C. Sulfur vapor was found to be a milder and better reductant than CO. Complete utilization of sulfur vapor, 90 pct K extraction, and 85 pct Al extraction were achieved. Alunite pellets having sufficient strength and resistance to degradation were produced by combining a sized-feed mixture with a KOH binder.

Correlation of the roasting time data is poor, and more timed investigations are needed. Additional studies should be conducted on pellets produced from alunite dust using a KOH binder, which may be acceptable but may require longer reduction roasting time. Also, pelletizing of alunite ground to minus 20 mesh should be investigated. A PRU test program needs to be completed, to study pellet durability, roasting parameters, and recovery of acceptable K₂SO₄ and Al₂O₃ products further.

REFERENCES

1. Dow Chemical Co., Thermal Research Laboratory. JANAF Thermochemical Tables. NSRDS-NBS 37, 2d ed., 1971, 1141 pp., plus supplements.
2. Fleischer, A. The Kalunite Process. Trans. AIME, v. 159, 1944, pp. 267-279.
3. Kelley, K. K., C. H. Shomate, F. E. Young, B. F. Naylor, A. E. Salo, and E. H. Hoffman. Thermodynamic Properties of Ammonium and Potassium Alums and Related Substances, With Reference to Extraction of Alumina From Clay and Alunite. Bu-Mines TP 688, 1946, 104 pp.
4. Kostin, W. N. Roasting of Alunite (With Sulfur). W. Ger. Pat. 2,348,403, Apr. 25, 1974.
5. U.S. Bureau of Land Management. Alunite Final Environmental Statement. August 1977, 579 pp.

APPENDIX A.--OPERATING CONDITIONS

1. Pellet feed: 6.6 lb raw pellets (6.0 lb dry basis) charged to dehydration chamber per hour.
2. Temperature of pellet feed: 16° C (60° F).
3. Pellets discharge from dehydration chamber into reduction chamber at 650° C (1,202° F).
4. Dehydration process heat is generated by burning natural gas in a direct-fired heater operating at an estimated thermal efficiency of 90 pct. Combustion gas combined with secondary air enters the bottom of the dehydration chamber at 800° C (1,472° F) and exhausts from top of chamber at 150° C (302° F).
5. Dehydrated pellets enter reduction chamber at 650° C (1,202° F) and discharge through bottom at 550° C (1,022° F).
6. Reducing gas: S₂ vapor in N₂ carrier gas.
7. The S₂-N₂ mixture is preheated in an electric tube furnace and enters reduction chamber at temperatures ranging up to 800° C (1,472° F).
8. Gaseous reaction products discharge from the reduction chamber at 600° C (1,112° F).
9. Sensible heat released in cooling the N₂ carrier gas and alunite pellets provides endothermic reduction heat.
10. Thermal equilibrium is maintained by combustion gas in the annular space.

APPENDIX B. - HEAT BALANCE--DEHYDRATION

Heat required to eliminate free water:

Enthalpy of water vapor at 150° C (302° F)....	1,180 Btu/lb
Enthalpy of liquid water at 16° C (60° F).....	28 Btu/lb
Difference.....	1,152 Btu/lb

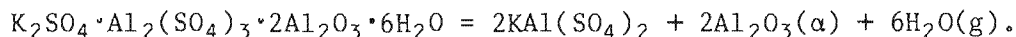
Heat required to vaporize 0.6 lb water:

$$1,152 \times 0.6 = 691 \text{ Btu.}$$

Heat required to raise temperature of 6 lb alunite ore to 650° C (1,202° F), with heat capacity of dry alunite ore assumed to be 0.26 Btu·lb⁻¹·°F⁻¹:

$$(1,202^\circ - 60^\circ \text{ F}) \times 0.26 \times 6 = 1,782 \text{ Btu.}$$

Heat required to dehydrate alunite (3):



$$H_T^\circ = 149,530 - 5.3 \text{ T.}$$

$$H_{923}^\circ = 149,530 - 5.3 (923),$$

$$= 149,530 - 4,892,$$

$$= 144,638 \text{ cal.}$$

Alunite ore sample contains 50 pct alunite: 6 lb dry ore contains 3 lb alunite.

$$1 \text{ g-mol alunite} = 828/454 = 1.824 \text{ lb.}$$

Heat required to dehydrate 3 lb alunite:

$$3/1.824 \times 144,638 = 237,891 \text{ cal.}$$

$$1 \text{ Btu} = 252 \text{ cal.}$$

$$237,891/252 = 944 \text{ Btu.}$$

Heat recovered from dehydration water in cooling from 650° C (1,202° F) to dehydration exhaust temperature, 150° C (302° F):

Enthalpy of water vapor at 650° C (1,202° F)....	1,637 Btu/lb
Enthalpy of water vapor at 150° C (302° F).....	1,180 Btu/lb
Difference.....	457 Btu/lb

Weight of dehydration water:

$$\frac{6 \times 18}{454} \times \frac{454}{828} \times 3 = 0.39 \text{ lb.}$$

Heat recovered:

$$457 \times 0.39 = 179 \text{ Btu.}$$

Total theoretical heat required to dehydrate 6.6 lb ore:

$$691 + 1,782 + 944 - 179 = 3,238 \text{ Btu.}$$

Thermal efficiency (combustion gas plus dehydration):

$$0.9 [(1,472^\circ - 60^\circ \text{ F}) - (300^\circ - 60^\circ \text{ F})] 100 / (1,472^\circ - 60^\circ \text{ F}) = 74.7 \text{ pct.}$$

Gross heat required:

$$3,238 / 0.747 = 4,335 \text{ Btu.}$$

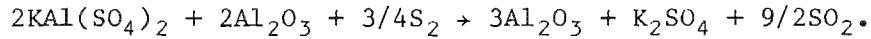
Natural gas required:

$$1,000 \text{ Btu} = 1 \text{ ft}^3.$$

$$4,335 / 1,000 = 4.33 \text{ ft}^3.$$

APPENDIX C. - HEAT BALANCE--REDUCTION

Sulfur reduction of dehydrated alunite may be expressed by the reaction:



For a reduction temperature of 600° C (1,112° F) (data from table C-1),

$$\begin{aligned} H_{873}(\text{reaction}) &= 3\Delta H_{873}(\text{Al}_2\text{O}_3) + \Delta H_{873}(\text{K}_2\text{SO}_4) + 9/2\Delta H_{873}(\text{SO}_2) \\ &\quad - 2\Delta H_{873}[\text{KAl}(\text{SO}_4)_2] - 2\Delta H_{873}(\text{Al}_2\text{O}_3) \\ &\quad - 3/4\Delta H_{873}(\text{S}_2), \\ &= -1,156,500 - 317,050 - 289,584 + 1,107,070 \\ &\quad + 771,000 - 26,772, \\ &= -1,789,906 + 1,878,070, \\ &= 88,164 \text{ cal} = 350 \text{ Btu.} \end{aligned}$$

Sulfur gas required to reduce dehydrated alunite (basis: 1 h) (6 lb dry ore contains [6 - (3 + 0.39)] = 2.61 lb dehydrated alunite):

$$2.61 \times 454 = 1,185 \text{ g.}$$

$$\text{Mol wt } [2\text{KAl}(\text{SO}_4)_2 + 2\text{Al}_2\text{O}_3] = 720.3 \text{ g/mol.}$$

Moles S₂ required:

$$1,185/720.3 \times 0.75 = 1.23 \text{ g-mol.}$$

Heat required to reduce 2.61 lb dehydrated alunite:

$$1,185/720.3 \times 88,164 \text{ cal/mol} = 145,043 \text{ cal} = 576 \text{ Btu.}$$

Sensible heat recovered from cooling ore (dehydrated ore--5.61 lb--enters reduction chamber at 650° C (1,202° F) and exits at 550° C (1,022° F)):

$$5.61 \text{ lb} \times 180^\circ \text{ F (temp. drop)} \times 0.26 \text{ Btu}\cdot\text{lb}^{-1}\cdot^\circ\text{F}^{-1} = 263 \text{ Btu.}$$

Heat to be supplied by reduction carrier gas:

$$576 - 263 = 313 \text{ Btu.}$$

SULFUR REQUIREMENT

$$1.23 \text{ mol S}_2 \times 64/454 = 0.17 \text{ lb/h S}_2.$$

$$0.17 \times 359/64 = 0.95 \text{ ft}^3/\text{h (STP)},$$

where STP is standard temperature and pressure.

NITROGEN REQUIREMENT

At 650° C (1,202° F) inlet temperature:

$$313 \text{ Btu} / [0.25 \text{ Btu} \cdot \text{lb}^{-1} \cdot ^\circ\text{F}^{-1} \times 90^\circ \text{ F (temp. drop)}] = 13.9 \text{ lb/h N}_2.$$

$$13.9 \times 359/28 = 178 \text{ ft}^3/\text{h (STP)}.$$

At 800° C (1,472° F) inlet temperature:

$$313 \text{ Btu} / [0.25 \text{ Btu} \cdot \text{lb}^{-1} \cdot ^\circ\text{F}^{-1} \times (1,472^\circ - 1,112^\circ \text{ F})] = 3.5 \text{ lb/h N}_2.$$

$$3.5 \times 359/28 = 44.9 \text{ ft}^3/\text{h (STP)}.$$

SO₂ IN EXHAUST GAS

At 650° C (1,202° F) inlet temperature (assuming reduction reaction goes to completion), S₂ in carrier gas:

$$0.95 / (178 + 0.95) 100 = 0.53 \text{ pct.}$$

$$0.53 \times 4.5 / 0.75 = 3.18 \text{ pct SO}_2.$$

At 800° C (1,472° F) inlet temperature, S₂ in carrier gas:

$$0.95 / (44.9 + 0.95) 100 = 2.07 \text{ pct.}$$

$$2.07 \times 4.5 / 0.75 = 12.4 \text{ pct SO}_2.$$

TABLE C-1. - Thermodynamic data

Substance	H ₈₇₃ ^o -H ₂₉₈	ΔH ₂₉₈ ^o	ΔH ₈₇₃ ^o = ΔH ₂₉₈ ^o + (H ₈₇₃ ^o -H ₂₉₈ ^o)	Ref.
KAl(SO ₄) ₂	35,635	-589,170	-553,535	3
Al ₂ O ₃ (α).....	14,900	-400,400	-385,500	1
S ₂ (ideal gas)...	4,856	30,840	35,696	1
SO ₂ (ideal gas)..<	6,595	-70,947	-64,352	1
K ₂ SO ₄	25,620	-342,670	-317,050	3