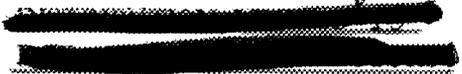




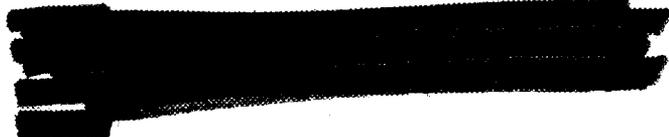
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Evaluation of Potential Processes for the Recovery of Resource Materials from Coal Residues: Fly Ash

V. A. DeCarlo
F. G. Seeley
R. M. Canon
W. J. McDowell
K. B. Brown



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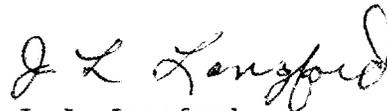
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CHEMICAL TECHNOLOGY DIVISION

EVALUATION OF POTENTIAL PROCESSES FOR THE RECOVERY OF
RESOURCE MATERIALS FROM COAL RESIDUES: FLY ASH

V. A. DeCarlo
F. G. Seeley
R. M. Canon
W. J. McDowell
K. B. Brown



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Date Published: March 1978

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EVALUATION OF POTENTIAL PROCESSES FOR THE RECOVERY OF
RESOURCE MATERIALS FROM COAL RESIDUES: FLY ASH

V. A. DeCarlo R. M. Canon
F. G. Seeley W. J. McDowell
K. B. Brown

ABSTRACT

This report evaluates potential processes for the recovery of resource materials from fly ash and presents preliminary experimental results. In the study presented here, existing processes such as lime-sinter and acid leach for the production of alumina and other resource materials from fly ash were investigated. Also, several new sinter-leach methods were studied; and a NaCl-Na₂CO₃ sinter, H₂O-acid leach method was found to produce >97% solubilization of aluminum, iron, and a number of trace elements such as titanium, uranium, and manganese. Conceptual process flowsheets were developed for three of the processes that appear to have merit: lime-soda-sinter, salt-soda-sinter--nitric acid leach, and nitric acid leach. Material balances for these processes, based on information available in the literature and from results of our investigations, are presented along with very preliminary cost estimates to be used for comparison purposes only at this stage of development. The cost estimates indicate reasonable agreement in the capital costs for the three plants; however, the operating costs and income from products show significant differences. Income from products is difficult to estimate at this stage of development. Material balances show that the recovery of alumina is ~85, 90, and 65% and the quantity of fly ash consumed is ~90, 60, and 30% for the lime-soda-sinter, salt-soda sinter--nitric acid leach, and the nitric acid leach processes respectively. The lime-soda-sinter process limits product yield to iron, alumina, and cement. The salt-soda-sinter--nitric acid leach and nitric acid leach processes are much more flexible in this regard. In addition to iron and alumina, they are adaptable to produce titanium, silica, and manganese, using solvent extraction methods as shown in our conceptual process flowsheets; various other metals and minerals can also be obtained, depending on the type of process treatment applied. Also, specific research and development requirements for further work are given in this report.

1. INTRODUCTION

The total ash collected in the United States in 1975, 60×10^6 tons, consisted of 42.3×10^6 tons of fly ash, 13.1×10^6 tons of bottom ash, and 4.6×10^6 tons of boiler slag (see Fig. 1). The percent utilization of fly ash, bottom ash, and boiler slag is 10.6, 26.7, and 40.0 respectively. It is obvious from these statistics that fly ash presents the greatest disposal problem. As shown in Table 1, only six other minerals are produced in larger quantities than coal ash. This quantity of ash presents a significant waste disposal problem but, if processed, could become a source of valuable minerals. Recovery of resource materials from this waste would also decrease the volume of ash requiring disposal. Furthermore, the dependence of our nation on imported alumina, a problem of both strategic and economic importance, would be reduced. The objectives of the work reported here were to study and evaluate existing techniques and to develop proposed and new techniques for processing the ash. The experimental program includes studying possible processing techniques followed by development and testing of critical process steps in candidate processes on a laboratory scale for aid in identifying the optimum process flowsheet and for providing the necessary design data for a cost estimate of the process.

The United States has large deposits of clays and ores which contain the same, or even somewhat larger, concentrations of some of the resource materials such as alumina. However, utilization of such deposits may become expensive when the costs associated with mine development, waste disposal, and environmentally acceptable restoration of the mined areas

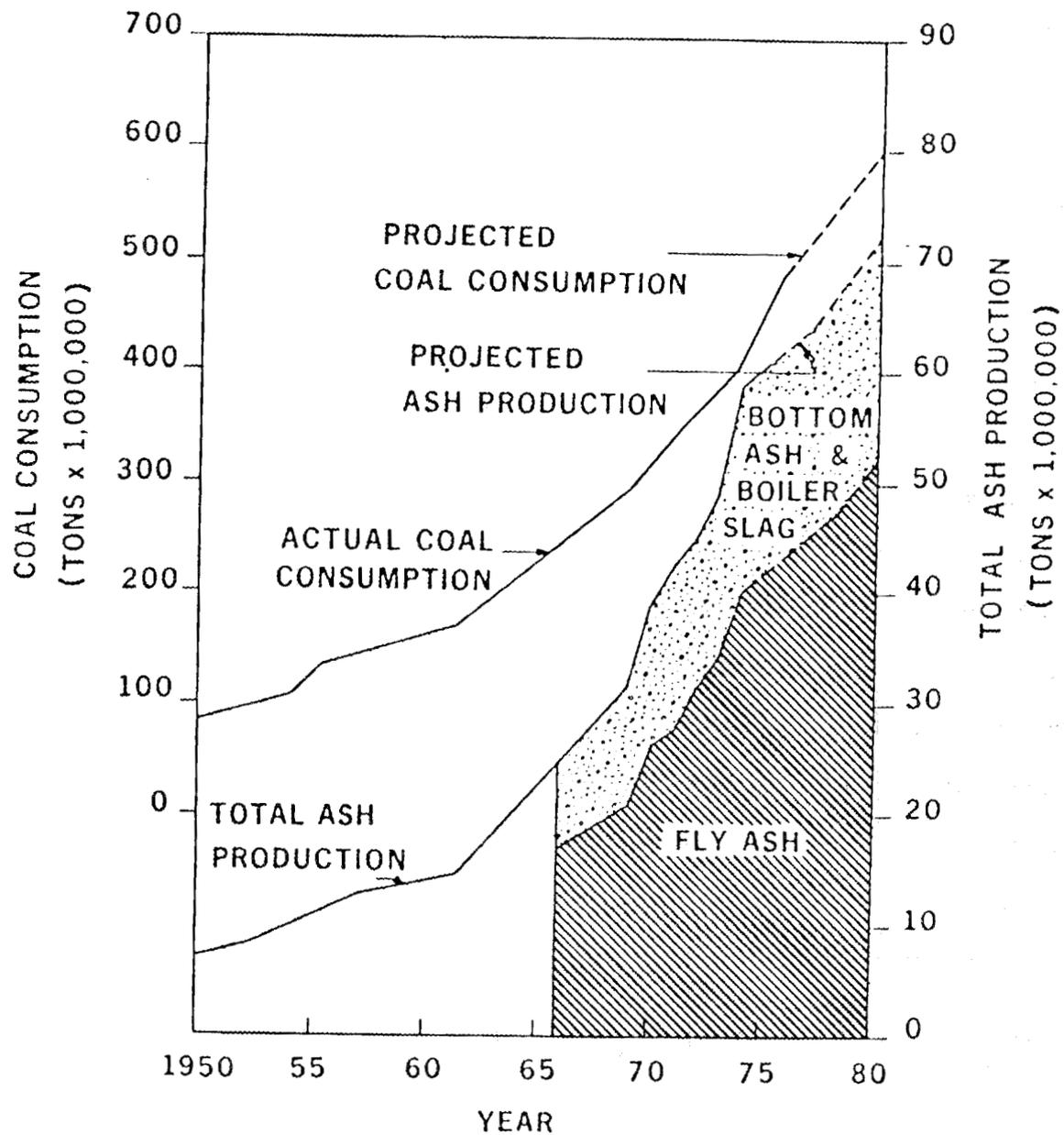


Fig. 1. Coal consumption and ash production by U.S. electric utilities.

Table 1. Production of minerals and solid mineral fuels in the United States^a

	Millions of short tons		
	1972	1973	1974
Stone	920.4	1060.1	1043.5
Sand/gravel	914.3	983.6	978.7
Coal (all types)	602.4	598.5	610.0
Iron ore	77.8	90.6	84.9
Portland cement	77.9	82.7	75.9
Clays	59.4	64.3	60.7
Coal ash	46.3	49.3	59.5
Salt	45.0	43.9	46.5
Phosphate rock	40.8	42.1	45.6
Slag (air-cooled)	25.0	28.8	29.8
Lime	20.2	21.0	21.6
Gypsum	12.3	13.5	11.9

^aData taken from Minerals Yearbook, Vol. 1, "Metals, Minerals, and Fuels," U.S. Dept. of Interior, 1974.

are taken into consideration. Most of these costs are either avoided in processing coal ash or are already included in the power/fuels generating costs.

The basic difficulties associated with processing fly ash for mineral recovery arise from the very high temperatures (e.g., 1750°C) to which the ash has been fired and the complex structure of the residue (i.e., interlocking molecular bonds with silicon). Breaking these interlocking bonds is the key to recovery of the minerals. Electron microscope photographs of fly ash, which can best be described as powdered glass beads, are shown in Figs. 2-5.

The concept of recovering resource materials from coal residues is not new since a review of the references and patents on the subject indicate that considerable work in this area was done well over 50 years ago. On the other hand, certain conditions exist today that make such technology development much more attractive than before; for example, the bulk of our nation's aluminum needs, excluding recycled material, is met by the importation of ores from countries belonging to a cartel. Next to the OPEC cartel, the International Bauxite Association (IBA) presents the most serious cartel threat to the United States. Ten countries that produce over 65% of the world's output and account for 80% of the bauxite/alumina trade are members of the IBA. Recent activities by some members of the IBA include large price increases, which reflect a monopolistic position as suppliers of this valuable ore instead of a market demand. Such a situation makes coal ash processing techniques for alumina recovery more attractive. Several other recoverable minerals, some in trace amounts, are also of interest.

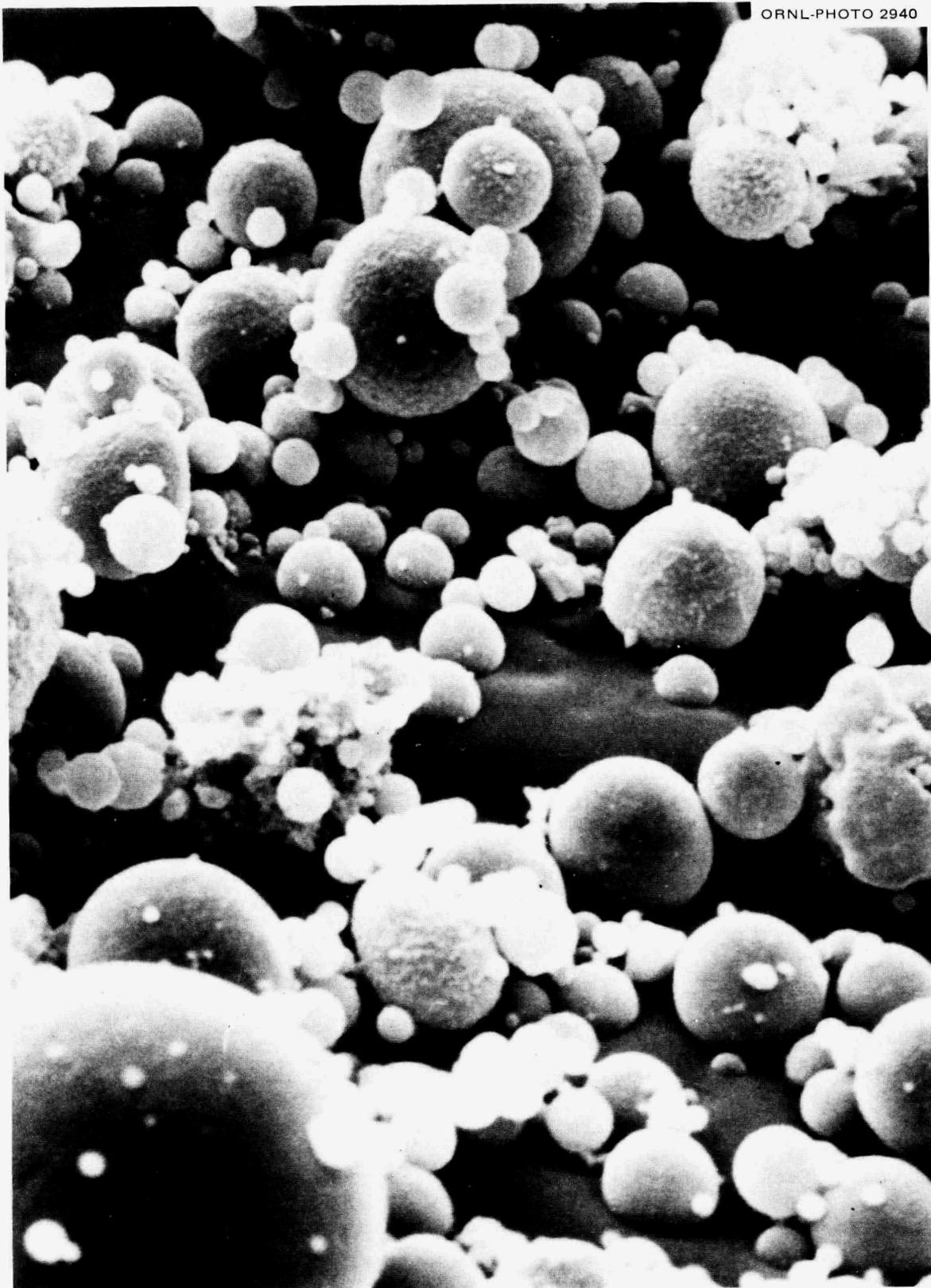


Fig. 2. Fly-ash particles, enlarged 1000X.

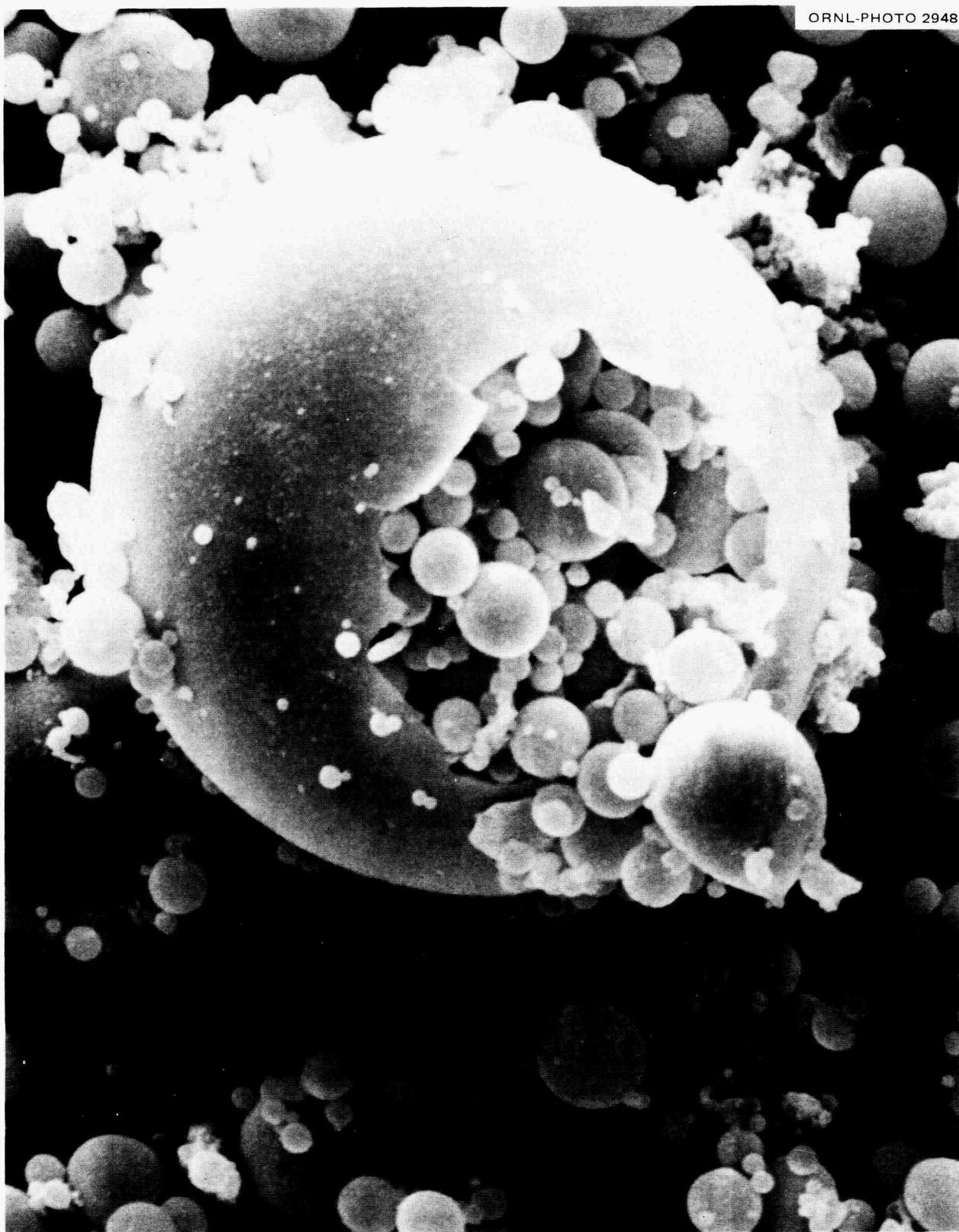


Fig. 3. Pluralsphere in fly ash, enlarged 1000X.

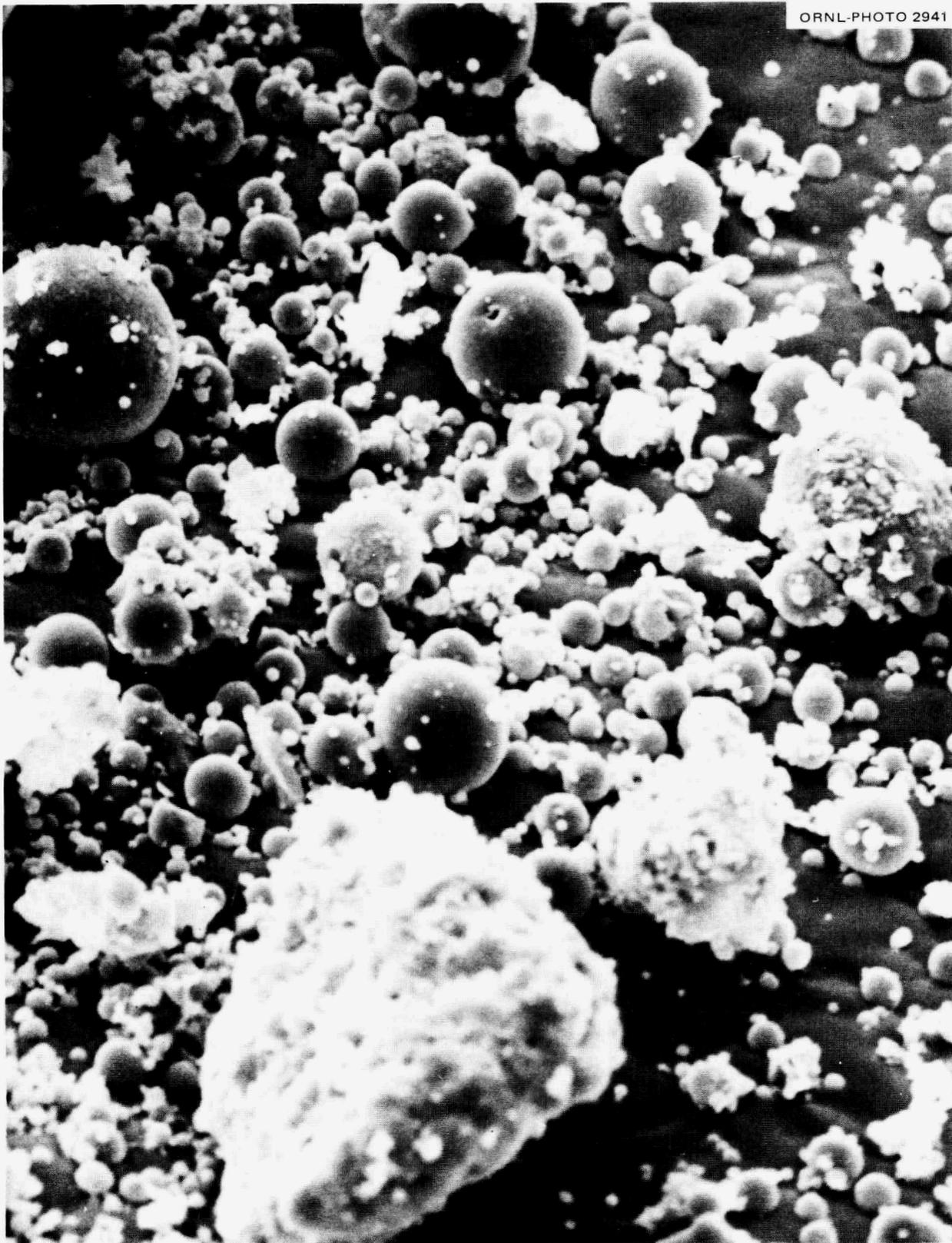


Fig. 4. Irregularly shaped fly-ash particles, enlarged 300X.

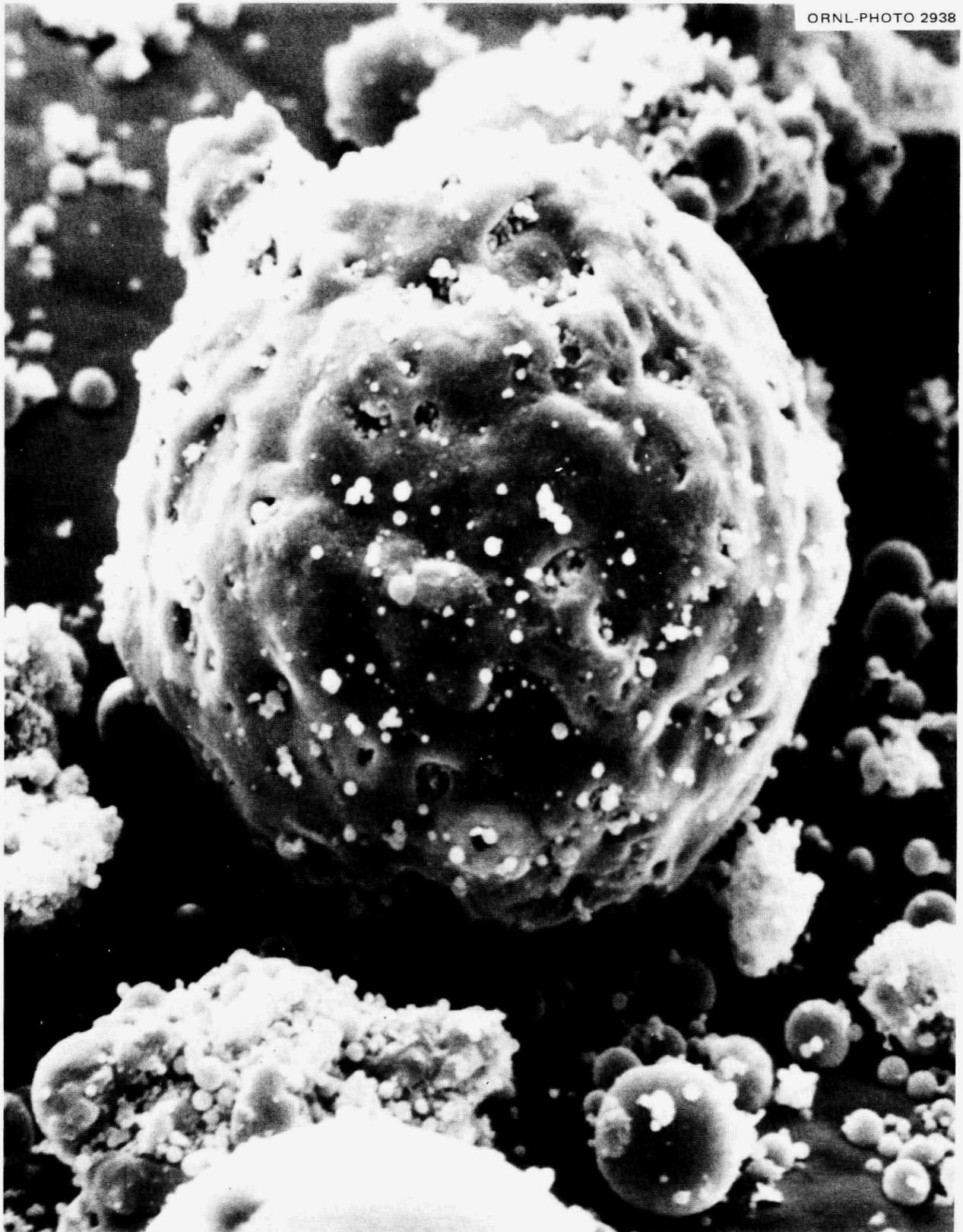


Fig. 5. Porous fly-ash particle, enlarged 300X.

A second circumstance prompting the development of ash utilization technology is the general desire to reduce environmental pollution through the increased utilization and recycle of waste materials generated by present industrial activities. Recent actions from environmentalists suggest certain leachable materials may need to be removed from ash dumps. This would require a limited treatment of the ash which could be extended to recover other resource materials, depending on the evaluation of economic and technical factors. This is also a potent force which tends to prevent the exploitation of new sources of low-grade ores for the production of these minerals.

The only existing methods of fly-ash resource recovery that have been demonstrated on an engineering scale are the lime-sinter and lime-soda-sinter (LSS) processes. These methods are now receiving considerable attention in the literature, but to our knowledge there are no commercial plants in operation. If 34×10^6 tons of the fly ash were processed by LSS, we would produce 62×10^6 tons of cement or 80% of the total U.S. production. Since the process requires a 2:1 ratio of limestone to fly ash, 68×10^6 tons of quality limestone (or 30% of the present U.S. production of cement limestone) would be required. The process would also produce 8×10^6 tons of alumina, or 50% of the U.S. demand. Such quantities of alumina and cement would affect the prices of these commodities; consequently, the consumption of large quantities of the current fly-ash production may not be possible. The process appears to have merit, however, and the market could probably absorb as much as 20% of the alumina and cement; and 16% and 10% of the U.S. demand for alumina and cement, respectively, would be met by consuming 6.76×10^6 tons of fly

ash. Distances between consumer, limestone mines, and fly-ash supply would determine the optimum location of an LSS plant.

In these processes, the fly ash is sintered with the indicated materials and then leached with soda ash (Na_2CO_3) solutions. We examined these procedures, as well as a variety of other sinter and fusion methods which we developed, followed by acid leaching. In all of the acid leach work, consideration was given to solvent extraction techniques as well as other separation operations as potential methods for recovering metal values from the leach liquor. Many of these methods would likely extract elements present only as trace material in the fly ash, such as uranium, manganese, and titanium in eastern ores and copper and molybdenum in western ores, with some additional expense. We are thus including uranium and titanium in our analyses as indicators of these types of trace metals.

The program is considered to have four parts, or phases, which will ultimately require the cooperation and interaction of the Oak Ridge National Laboratory, the Tennessee Valley Authority, and an industrial participant.

Phase I. A survey of the literature, based on existing bibliographies and other pertinent sources, was made in order to identify proposed processes for the recovery of various materials from coal utilization residues. An evaluation of the relative extent of technical development required for each process was made based on the quantity of available laboratory data and the existence of pilot-plant operation experience. From these results, we determined what specific information was required to aid in the development of various processes to produce resource materials. As an example, the presence of silica and iron in the fly ash

introduces different processing problems, depending on whether acid or alkaline methods are employed. In the acid methods, much of the iron dissolves while most of the silica remains insoluble. Thus, the acid processes must include procedures for removing the iron or converting it to an insoluble form. The alkaline processes must deal similarly with the silica. One real advantage of the alkaline processes is that mild steel can be used, whereas acid-resistant equipment is required for the acid systems.

Phase II. We are currently engaged in this phase of the program. Our tasks are to identify the processes that appear promising and apply physical techniques to develop these processes on a laboratory scale. Experimental work has been conducted to define variables and to determine the effectiveness of various separation techniques such as solvent extraction and magnetic and gravitational methods. These fundamental studies will form the basis for further development of continuous processing techniques. An attempt was made during this phase to select candidate processes for cost evaluation that appeared to be most feasible from both a technical and an economic point of view. The experimental program attempted to develop these processes for the purposes of optimizing process flowsheets and providing the necessary design data for process scale-up. Three processes were selected: lime-soda-sinter, salt-soda sinter--nitric acid leach, and nitric acid leach. A preliminary cost estimate was prepared for each.

Phase III. The results of Phase II will be used as a basis for additional work and will be utilized by a more applied minerals recovery process development program. Hopefully, this will generate the necessary data for a detailed engineering design of a bench-scale experiment.

Phase IV. Based on operating data obtained from laboratory bench-scale experiments, a demonstration plant would be designed and proposed for construction near one of TVA's power-generation facilities. Production-scale process plants should be located near large coal burning plants to provide a concentration of source material and to avoid transportation costs. Large TVA plants generate $\sim 1 \times 10^6$ tons of waste residue per year. It is anticipated that ORNL would provide part of the overall project management and perform the necessary laboratory support work as the project development continued in this phase of the program. TVA would provide a suitable site and process feed material, while the primary project management function would be fulfilled by the TVA and an industrial participant.

2. PROCESSES EXAMINED

2.1 Lime-Sinter Process

The lime-sinter process removes alumina from a refractory aluminosilicate compound with a reagent (i.e., calcium oxide from limestone) which has a stronger affinity for silica than does alumina. This is a modification of a process patented by Pedersen^{1,2} for smelting bauxite, limestone, iron ore, and coke to produce iron and calcium aluminate slag. A variation of the process was patented by Seailles and Dyckerhoff³ for sintering a mixture of limestone and high-silica alumina compound to form calcium aluminate.

Investigators^{4,5} have found that the calcium oxide:silica weight ratio should be 2 with sufficient calcium oxide to give a $\text{CaO}:\text{Al}_2\text{O}_3$ weight ratio of 5:3 in order to release alumina from silicated compounds.

The lime-sinter process has been the subject of considerable research by Murtha et al.,⁶ as well as Grim, Machin, and Bradley.⁷ Some of the work done on clays indicated an optimum sintering temperature range of 1370 to 1390°C.

The process development reported here first attempted to duplicate experiments reported in the literature; then parameters were varied in an attempt to increase the yield of alumina. Unfortunately, we were unable to achieve our objective. Figure 6 shows the sequence of operations of the process.

A cost estimate of this process was not made because of the greater yield of alumina from the lime-soda-sinter process. (The cost estimate for the lime-soda-sinter process is presented in Appendix A.)

2.1.1 Equipment and procedure

The fly ash used in these tests was obtained from the TVA Kingston Steam Plant; its analysis is given in Table 2. Although the material was received dry, it was slurried with water to represent the form of the ash that is being suggested as the process feed.

2.1.2 Magnetic separation

Some existing processes use a preliminary magnetic iron separation step in an effort to mitigate the problem of removing iron from the alumina and to provide a lower iron level in cement. In our work, we employed various techniques to determine an effective means for removing magnetic iron from fly ash. The most suitable method, with the available equipment, appeared to be a wet separation followed by drying of the two fractions. The fly ash was slurried with water and placed in a

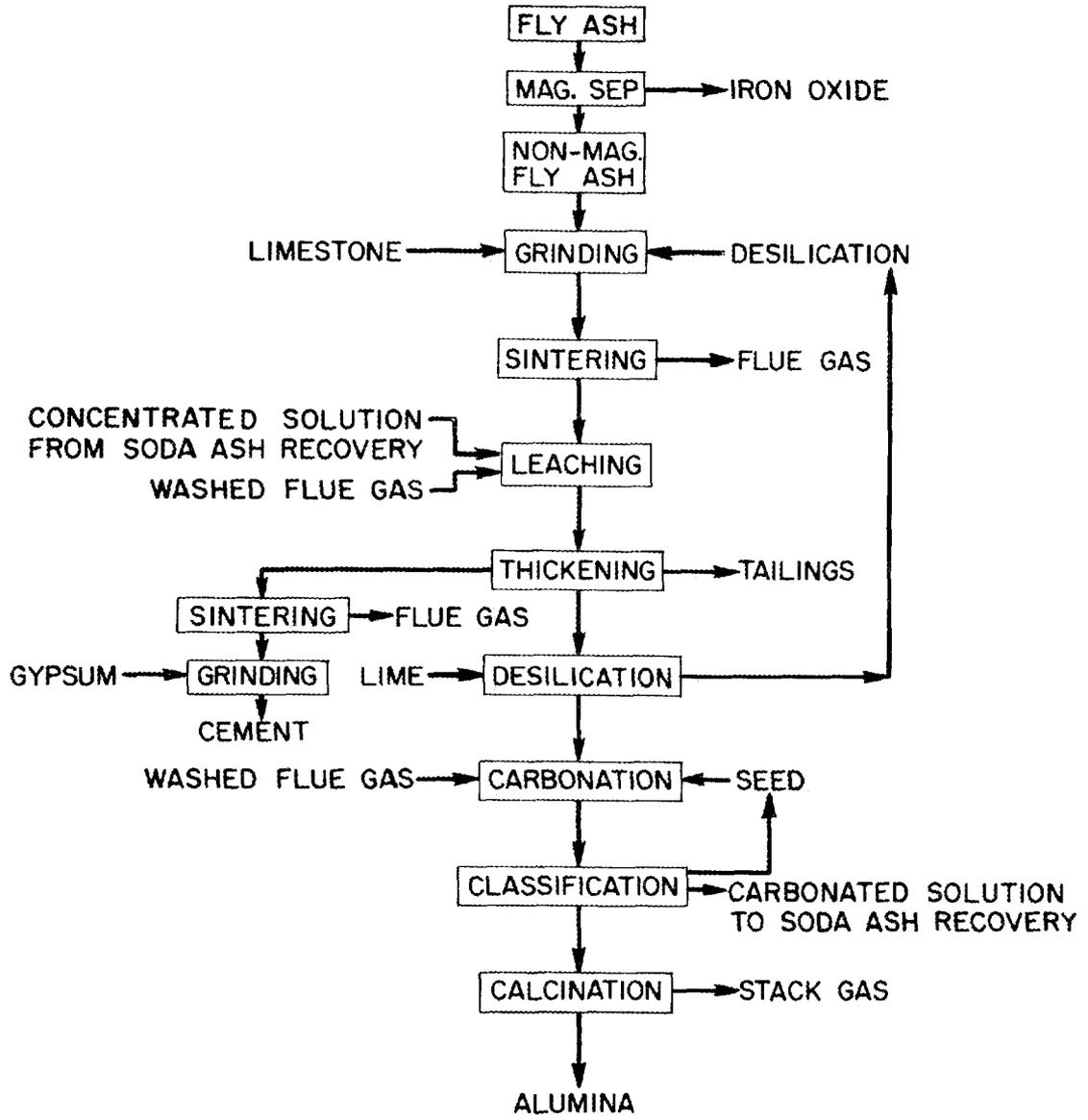


Fig. 6. Lime-sinter process.

Table 2. Analysis of fly ash from TVA Kingston Steam Plant

Constituent	wt %	Constituent	wt %	Constituent	ppm
SiO ₂	49.4	Si	23.1	Ba	38
Al ₂ O ₃	27.96	Al	14.8	Cr	129
Fe ₂ O ₃	10.77	Fe	7.53	Co	50
MnO ₂	0.30	Mn	0.19	Ni	221
CaO	1.51	Cu	1.08	Rb	245
MgO	1.38	Mg	0.83	S	1800
TiO ₂	1.68	Ti	1.01	Sr	880
K ₂ O	3.14	K	2.61	V	180
				Zn	233

separatory funnel surrounded by permanent magnets outside the glass surface. The more magnetic particles, which contained a higher percentage of iron, were retained on the inside surface of the glass. The ash was recycled six times. Approximately 10 kg of the fly ash has been processed in this manner to provide fly ash low in magnetic iron for those studies in which a low-iron fraction appeared to be an advantage. Upgrading of the magnetic fraction would provide a salable product. The following table summarizes typical data obtained by use of this method for removing magnetic iron from fly ash:

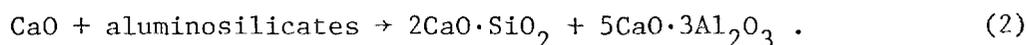
	<u>Before magnetic separation</u>	<u>After magnetic separation</u>	
		<u>Magnetic fraction</u>	<u>Nonmagnetic fraction</u>
Weight, g	100	12	86
Fe, g	7.21 (100%)	3.74 (52%)	3.50 (48%)
K, %	2.54 (100%)	0.17 (7%)	2.2 (87%)

Although 52% of the total iron was removed by this procedure, the iron-rich fraction is not a salable product because blast furnace feed specifications require 60% iron content and <0.15% potassium. Because the magnetic separation step is simple and the less-magnetic fraction of the fly ash is more suitable for cement manufacture, it is apparent that additional research is warranted. More efficient iron recovery is possible,⁶ but the problem of potassium separation has not been resolved. The economics would need to be evaluated after the cost of upgrading the iron oxide has been calculated to determine whether the process should be included in a final flowsheet.

2.1.3 Sintering

The wet, nonmagnetic fly-ash fraction was partially dried and mixed with a calculated quantity of CaCO_3 to give $\text{CaO}:\text{Al}_2\text{O}_3$ and $\text{CaO}:\text{SiO}_2$ mole ratios of 1.79 and ~ 2.0 respectively.⁸ Mixing took place during wet grinding of the material to -100 mesh. After four attempts, a mixture was prepared which self-disintegrated when cooled after sintering at 1380°C for 1-1/2 hr. Self-disintegration of the sinter is considered desirable to eliminate the necessity of additional grinding. Rapid cooldown of the sintered mix apparently aided self-disintegration. The furnace allowed the sample to be heated to 1380°C in 2 hr and cooled so that it could be removed in 2 hr at 200°C .

The chemical reactions that occur are:

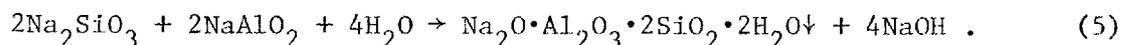
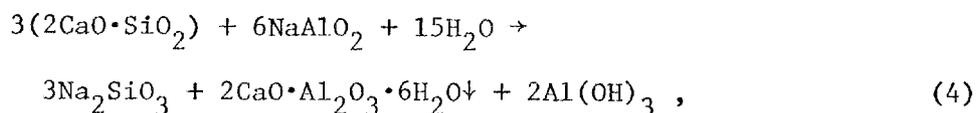
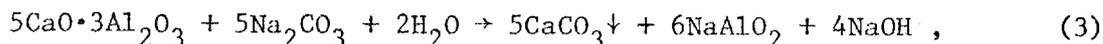


The sintering temperature was not varied because the literature⁶ indicated that sintering at 1380°C allowed the largest percent of soluble alumina to be recovered. The reaction time was varied between 1 and 3 hr in an effort to promote self-disintegration, which occurred at a reaction time of 1-1/2 hr; however, more research is needed to optimize this step.

2.1.4 Leaching

The weight loss during sintering is $\sim 30\%$, due primarily to loss of moisture and CO_2 . The sintered ash was leached for 15 min at 65°C with a 3% solution of Na_2CO_3 to provide 1.66 moles of Na_2CO_3 for each mole of Al_2O_3 present in the material.⁷ (The Na_2CO_3 solution can be recycled

from a soda ash recovery section.) To maintain the proper concentrations of soda, alumina, and carbonate in the pregnant liquor, CO₂ gas was added to the solution during leaching. The mixture was filtered, and the filtrate was washed free of soluble soda, alumina, and carbonate. The chemical reactions that occur are believed to be:



Reaction (3) is the most desirable; however, the other two reactions also occur. Based on analyses of the filtrate and the residue of one run, the best yield of alumina extracted was 56.6 and 67.2% respectively. Further research is needed to optimize the leaching conditions to increase the yield of alumina.

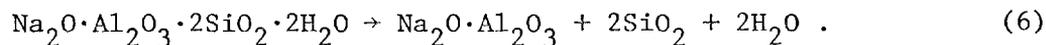
2.1.5 Cement

The tailings of the Na₂CO₃ leaching were sintered at 1094°C for 2 hr, which removed all of the water and CO₂. The sintering temperature and reaction time are the same as those used for the production of Portland cement. The material from this second sinter formed clinkers. A quantity of gypsum not to exceed 3 wt % of the resulting cement (which is the maximum quantity allowed) was added as CaSO₄ and subsequently mixed and ground. Water was then added to the cement to make concrete. The resulting product seemed reasonably strong but was not subjected to

any quantitative tests. The determination of optimum conditions to produce the best quality of cement was not included in this study because of time limitations; however, this would be a very important part of any further research.

2.1.6 Desilication

Desilication of the pregnant solution from the Na_2CO_3 leaching step is necessary because of the high concentration of silica in the solution. The lime for this step was obtained by calcining limestone at 1200°C . The lime was slurried with 10% of the pregnant liquor before it was added to the desilication step. The filtrate from the leaching step was mixed with calcined limestone. Calculations indicated that 0.5 wt % limestone would be required to desilicate the solution. The mixture was heated in an autoclave for 2 hr at 175°C and 200 psi. The conditions given in the literature⁹ for this step are a temperature of 175°C and a pressure of 100 psi. We decided to use a higher pressure in an attempt to increase the yield; however, our efforts were unsuccessful. The desilicated solution was cooled, filtered, and washed. The chemical reaction that occurs is as follows:

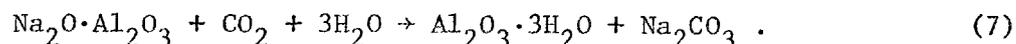


More research will be required in order to optimize the temperature and pressure for the reaction.

2.1.7 Carbonation

The desilicated solution was carbonated at 75°C for 24 hr by passing CO_2 through the solution. (The CO_2 gas used in this operation could be

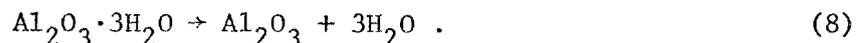
obtained from the sintering step.) Fine alumina trihydrate crystals were added as seed to aid in precipitation; an equivalent of 25 wt % of the alumina that precipitates is required.⁸ The filtrate was then washed and dried. The chemical reaction that occurs is:



This step is straightforward; the time at temperature could probably be reduced.

2.1.8 Calcination

The alumina trihydrate from the carbonation section was calcined at 1100°C for 2 hr to form alumina. The chemical reaction that occurs is:



This step is straightforward, and no further research is required.

2.2 Lime-Soda-Sinter Process

The first lime-soda-sinter process was developed by Adolf Kayser⁹ in 1902 to separate alumina from silica. In 1947, Conley¹⁰ developed a process for separating alumina from clay. During World War II, a 50-ton/day plant was built in Wyoming to produce alumina from anorthosite; however, it was never put into operation.

In the process we investigated, the fly ash is mixed with limestone and soda ash in a wet grinding step and the resulting mixture is sintered to convert the alumina to sodium aluminate and the silica to dicalcium silicate. The sintered product is leached with a dilute Na_2CO_3 solution to dissolve sodium aluminate from the sinter, and the resulting slurry

is processed to remove the residue from the leach liquor. The pregnant solution is treated with lime in an autoclave to precipitate dissolved silica, which is then removed by settling and filtration. The desilicated liquor is carbonated to precipitate alumina trihydrate, which is then separated from the liquor, washed, and calcined to produce alumina. The tailings from the leaching step are sintered and mixed with gypsum during grinding to form cement. An overall flowsheet of the sequence of operations is shown in Fig. 7. A cost estimate of this process is presented in Appendix A. The material balance flowsheets on which the cost estimate is based are also included in Appendix A (see Figs. A-1 through A-10).

2.2.1 Sintering

The fly ash was processed wet in a magnetic separation step (described in Sect. 2.1.2) to remove the magnetic fraction. The non-magnetic portion of the fly ash, ~85%, was partially dried and mixed with limestone and a soda ash solution in a wet grinding step to obtain a -200 mesh material. The quantities of limestone and soda added were sufficient to produce a mixture containing 1 mole of soda per mole of alumina and 2 moles of CaO per mole of silica. This method differs from the lime-sinter process in that the Na_2CO_3 is mixed with the fly ash plus CaCO_3 prior to sintering. The literature indicates that a significantly higher recovery of Al_2O_3 can be obtained using this method.⁷ The disadvantage is that the Na_2CO_3 must be washed from the residue prior to processing it into cement.

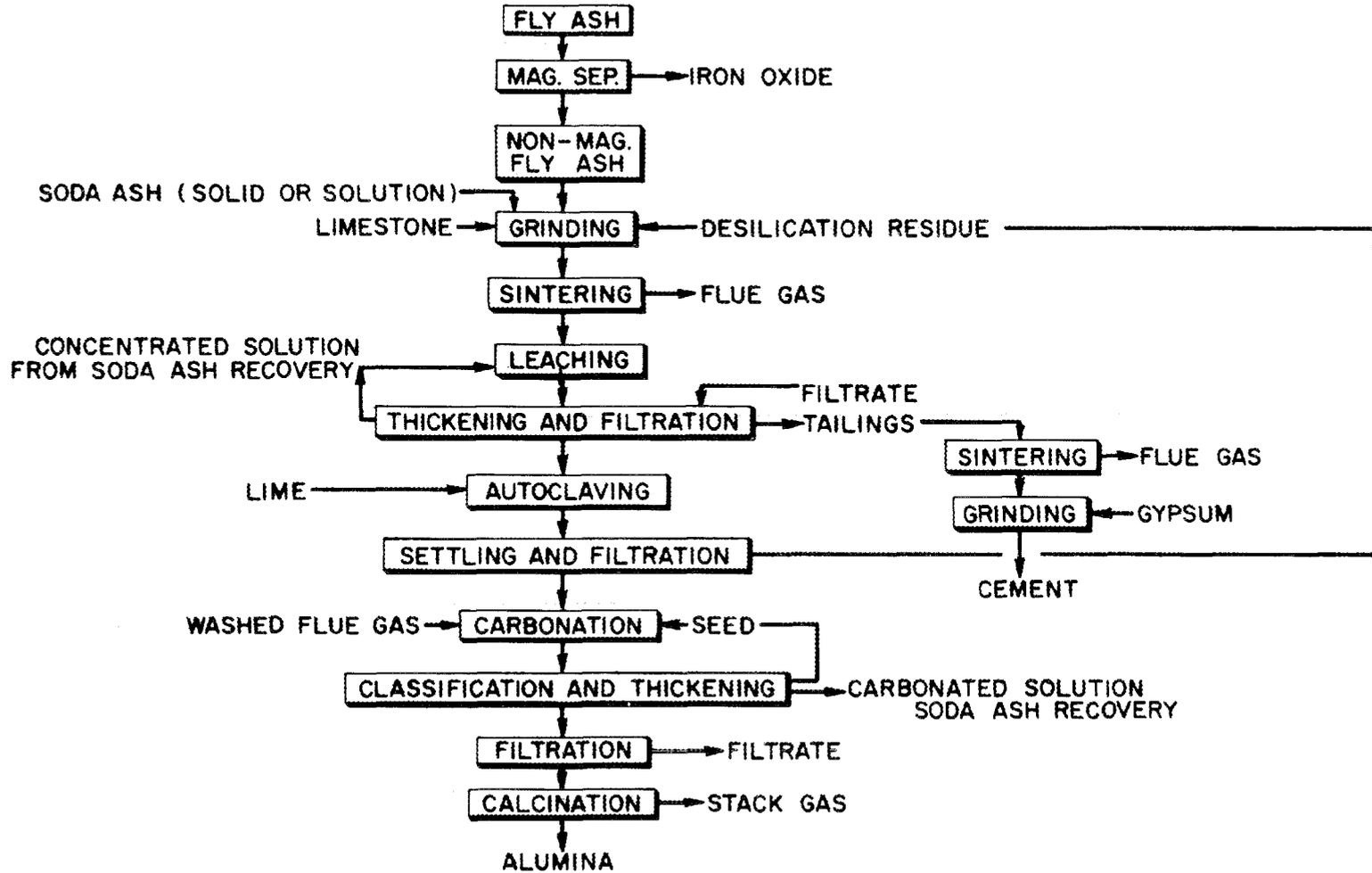
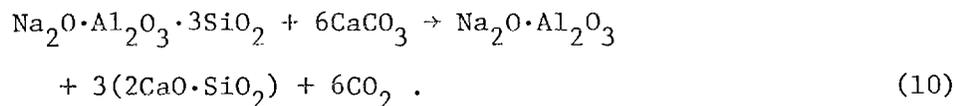
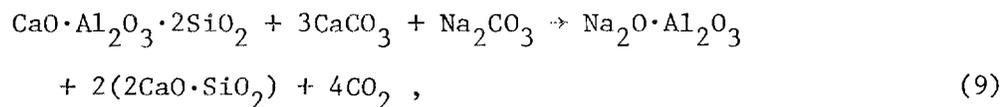


Fig. 7. Lime-soda-sinter process.

The first lime-soda-sinter (fly ash + limestone + Na_2CO_3) experiment was carried out at 1380°C with poor results. The mixture formed a glass-like melt that did not appear suitable for further processing because of the potential difficulty of grinding. Apparently, the sintering temperature was too high in this experiment. A second lime-soda sinter, which was performed at 1250°C for 30 min, was much more successful. Although it failed to self-disintegrate to a powder, it did form a grainy, cracked solid which was very easily ground with mortar and pestle to -65 mesh. Another sinter made under the same conditions gave the same result. The reactions that occur are believed to be:



Further research is required to optimize the sintering temperature and concentrations of limestone and sodium carbonate.

2.2.2 Leaching

A sample of the sintered product was mixed with a Na_2CO_3 solution and leached for 15 min at 95°C .¹¹ Approximately 2 g of leaching solution was found to be required per gram of sintered material. The slurry produced by leaching was filtered, and the residue was washed. (Part of the wash can be recycled to the leaching solution.) Four portions of the sintered product were leached, using different Na_2CO_3 concentrations and leach times. The results are given in the following table:

<u>Leach No.</u>	<u>Na₂CO₃ conc. (M)</u>	<u>Leach time (min)</u>	<u>Percent alumina recovered^a</u>
6A1	1.11	15	58.5
6A2	0.56	15	61.1
6A3	0.56	60	43.4
6A4	2.23	15	37.4

^aIn the filtrate.

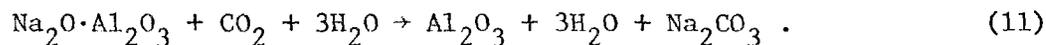
The steps following the sintering and leaching steps are similar to those of the lime-sinter process. Although time did not permit additional experimental work, the description of further process steps is included for general information and to aid in understanding the material balance flowsheets prepared for the cost estimate.

2.2.3 Desilication

The pregnant solution contains soluble silica, which must be removed before the alumina is precipitated as the trihydrate. When limestone is added and the mixture placed in an autoclave for 45 min at 174°C at 100 psi, 96% of the silica in solution reacts to form a precipitate ($2\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 5\text{H}_2\text{O}$). The mixture is then filtered to separate the residue from the desilicated solution, which can be recycled.

2.2.4 Carbonation

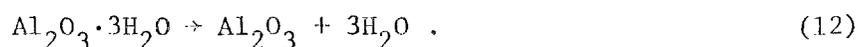
During the carbonation step, CO₂ is passed through the desilicated solution for 1 hr at 90°C. This precipitates about 87% of the alumina as alumina trihydrate. The chemical reaction is:



Alumina trihydrate seed, which comprises 30% of the alumina to be precipitated, is added to promote precipitation. The precipitate is filtered and washed.

2.2.5 Calcination

The alumina trihydrate from filtration is calcined for 90 min at 1094°C to produce alumina. The reaction is:



2.2.6 Cement

The tailings from the filtration step during leaching are sintered at 1094°C for 90 min -- a treatment which removes all of the H₂O and CO₂. The material from the sinter is in the clinker form. A quantity of gypsum not to exceed 3 wt % of the resulting cement product is added as CaCO₃ during grinding and mixing of the two materials.

2.3 Salt-Soda-Sinter--Nitric Acid Leach

As an alternative method for opening up the aluminum silicates in fly ash, the system NaCl--Na₂CO₃--fly ash was investigated. This is a new process developed at ORNL; however, a modification of a fusion method was first proposed by W. D. Arnold et al.¹² The fusion mixture, NaCl--Na₂CO₃ (2:1), was mixed with fly ash in a 3:1 ratio, heated to sintering temperatures of 700 to 1050°C, and then leached with various solutions. A programmed increase in temperature improved the leaching qualities of the sinter-cake; therefore, the procedure followed in the tests reported here provided for an initial temperature increase to 600°C (≈1 hr) and a subsequent rate of increase of 100°C per hour until the desired

sintering temperature had been attained. A 2-hr period at the maximum temperature was used in these tests; however, 0.5 to 1 hr would probably be adequate. The most effective treatment found was a sintering temperature of 1050°C and a combination of an initial H₂O leach of the sintercake followed by a nitric acid leach. Most of the unreacted NaCl and Na₂CO₃ can be recovered from the H₂O leach filtrate. Although the production of NaAlO₂ is expected in this fusion, <1% of the aluminum is solubilized in the H₂O leach even at a pH of 12 to 13. As yet, we have no explanation for this behavior. Substitution of Na₂CO₃ or NaOH solutions for the H₂O leach provided no more effective aluminum recovery than the H₂O. However, aluminum, iron, uranium, and titanium are all effectively solubilized in a dilute acid leach of H₂O-leached residue. Data for these sinter-leach tests are summarized in Table 3. In one of the tests, sulfuric acid was substituted for nitric acid in the second leach; these results are also included in the table. Aluminum recovery vs sintering temperature is shown graphically in Fig. 8. An overall flowsheet of the sequence of operations is shown in Fig. 9. A cost estimate of this process is presented in Appendix B. The material balance flowsheets for which the estimate was made are also given in Appendix B (see Figs. B-1 through B-9).

2.4 Other Sintering Methods

2.4.1 NaCl

In order to determine the effects of the individual components of the salt-soda-sinter on the recovery of aluminum from fly ash, a sample of the ash was heated at 1050°C with NaCl in the same manner as in the

Table 3. Summary of sinter-leach test data

Sintering conditions: fusion mixture contained 3 parts of NaCl-Na₂CO₃ (2:1) to 1 part of fly ash; programmed temperature increase of initial 600°C/hr followed by 100°C/hr; 2 hr at maximum temperature. Leaching time, 3 to 5 hr.

Initial wt of fly ash (g)	Sintering temp. (°C)	First leach					Second leach				
		Leaching agent	Temp. (°C)	Vol. (ml)	Residue wt (g)	Al leached (%)	Leaching agent	Temp. (°C)	Vol. (ml)	Residue wt (g)	Al leached (%)
25	1050	2 N H ₂ SO ₄	90	1000	23.1	97					
25	1050	2 N H ₂ SO ₄	85	1000	5.1	99.9					
25	1050	H ₂ O	85	1000	33.2	0.5	1 N HNO ₃	85	1000	6.5	98.7
25	1050	1 M Na ₂ CO ₃	85	1000	30.7	0.6	1 N HNO ₃	85	1000	0.7	99.9
25	1050	1 M NaOH	85	1000	30.5	13.0	1 N HNO ₃	85	1000	0.6	99.9
25	700	H ₂ O	85	1000	24.3	0.1	1 N HNO ₃	85	1000	19.6	36.4
25	800	H ₂ O	85	1000	28.0	0.1	1 N HNO ₃	85	1000	11.8	77.6
25	900	H ₂ O	85	1000	30.6	<0.1	1 N HNO ₃	85	1000	11.5	96.7
50 ^a	900	H ₂ O	85	1000	66.5	<0.1	1 N HNO ₃	85	1000	49.5	58.4
25	1050	H ₂ O	85	1000	34.0	0.5	1 N HNO ₃	100	1000	16.2	97.5
25	1050	H ₂ O	85	1000	34.6	0.4	1 N HNO ₃	100	1000	17.3	97.6
25	1050	H ₂ O	85	1000	33.5	0.4	1 N H ₂ SO ₄	100	1000	15.9	97.4

^aRatio of fusion mix to fly ash: 1.5/1.

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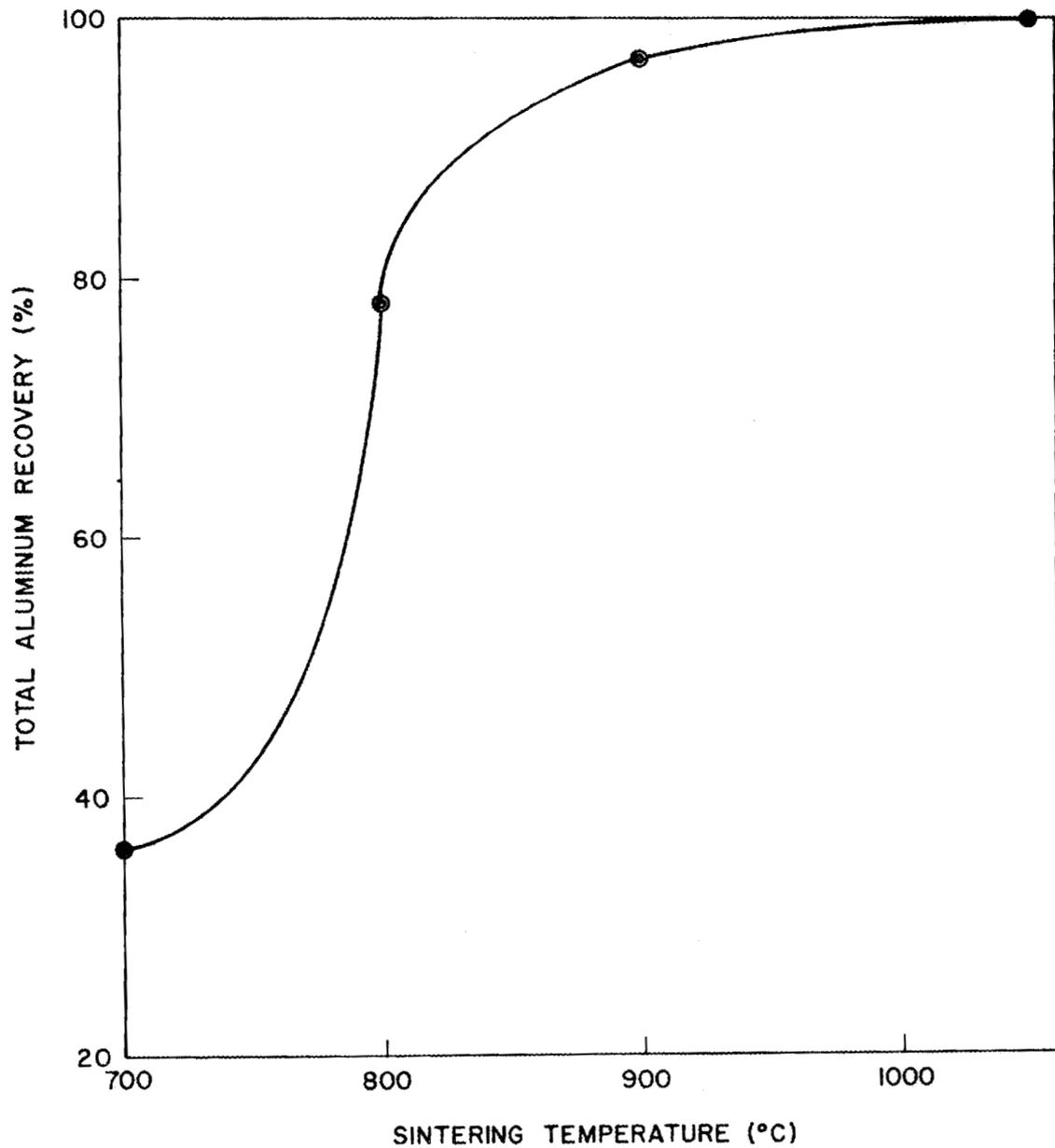


Fig. 8. Effect of sintering temperature on aluminum recovery.

Test conditions: programmed temperature increase, 2 hr at maximum temperature; fusion mix: 50 wt % NaCl, 25 wt % Na₂CO₃, 25 wt % fly ash; leaches: No. 1, H₂O; No. 2, 1 N HNO₃.

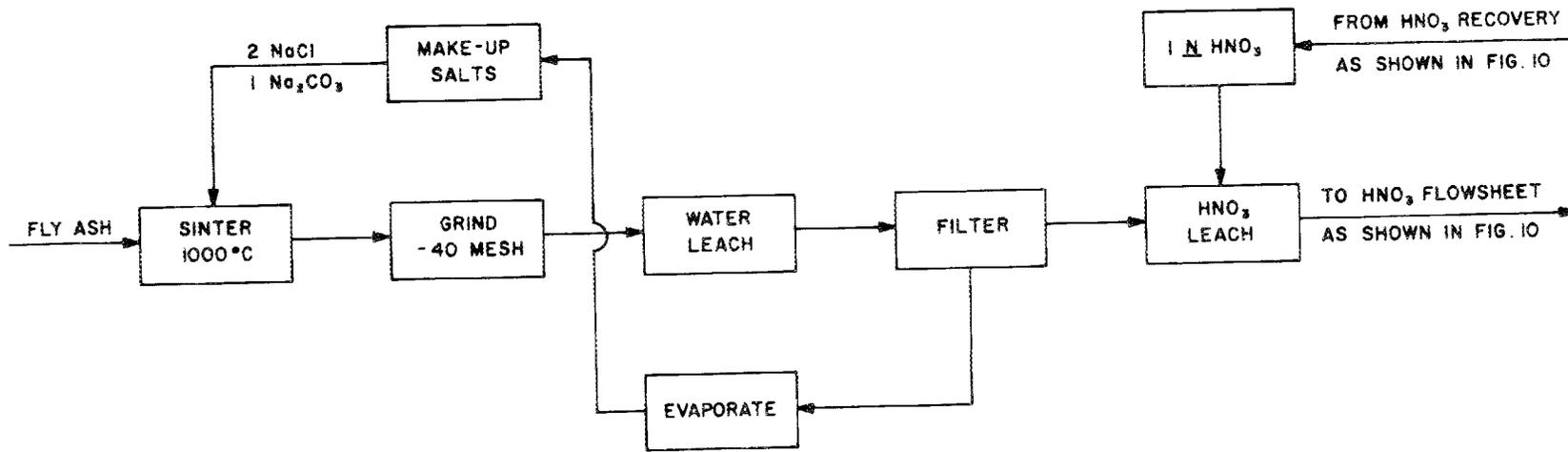


Fig. 9. Salt-soda-sinter process.

NaCl-Na₂CO₃ sinter tests. After these solids had been successively leached with 1 M Na₂CO₃ and 1 N HNO₃, the aluminum recovered from the residue was found to be only 27%. A similarly treated sample, leached first with 1 M NaOH and then with 1 N HNO₃, yielded a 45% aluminum recovery.

2.4.2 Na₂CO₃

Sintering fly ash with Na₂CO₃ in a 1:1 mixture at 1050°C followed by leaches with 1 N Na₂CO₃ and 1 N HNO₃ solutions gave an aluminum recovery of 66% and a weight loss of 40% of the air-dried solids. A similarly sintered sample leached successively with H₂O and 1 N HNO₃ provided an aluminum recovery of only 47% with an accompanying weight loss of 42%.

2.4.3 CaCl₂-Na₂CO₃

A sample of fly ash sintered with a 2:1 mixture of CaCl₂ and Na₂CO₃ at a 1:3 ratio at 1050°C for 2 hr, followed by successive leaches with H₂O and 1 N HNO₃, solubilized 78% of the aluminum found originally in the ash.

2.4.4 NaCl-CaCO₃

In a similar test, a sample of fly ash sintered with a 2:1 mixture of NaCl and CaCO₃ at a 1:3 ratio at 1050°C for 2 hr, followed by leaches with H₂O and 1 N HNO₃, solubilized 74% of the aluminum found in the ash.

2.4.5 CaSO₄

Although analytical material balances were poor, fairly high recoveries of uranium, aluminum, iron, and titanium were indicated after a

sample of fly ash had been sintered with CaSO_4 (1:2 ratio) at 1450°C for 3 hr, followed by a leach with concentrated H_2SO_4 at 40% solids at 90°C for 3 hr and dilution to $\sim 20\%$ solids with an additional 3-hr leach. Test data are shown in Table 4.

Table 4. Recovery of metal values from fly ash by sintering with CaSO_4 and leaching with H_2SO_4

Sintering conditions: 2:1 mixture of CaSO_4 and fly ash heated at 1450°C for 3 hr.

Leaching conditions: contacted with 36 N H_2SO_4 at 60% solids for 3 hr at 90°C and then diluted to $\sim 20\%$ solids and leached for an additional 3 hr at 90°C .

Weight loss (%)	Percent leached			
	U	Al	Fe	Ti
26	82	98	90	94

2.4.6 $\text{CaCl}_2\text{-CaSO}_4\text{-NaCl}$

Two samples of fly ash were fused at 700°C with a low-melting mixture containing CaCl_2 , CaSO_4 , and NaCl (mole % = 51.7, 2.7, 45.6). The ratio of the fusion mixture to fly ash was 2:1. The fused solids were leached with 2 N H_2SO_4 at 90°C for 5 hr at a pulp density of 20% solids. The recoveries of uranium, aluminum, iron, and titanium were only moderate to low. Data for these tests are shown in Table 5. Recoveries are based on an average of filtrate and leached solids analyses.

Table 5. Recovery of metal values from fly ash by low-temperature sintering with CaCl_2 - CaSO_4 - NaCl and leaching with H_2SO_4

Sintering conditions: 51.7-2.7-45.5 mole % CaCl_2 - CaSO_4 - NaCl mixed with fly ash in a 2:1 ratio, heated to 700°C for 3 hr.

Leaching conditions: sinter cake leached with 2 N H_2SO_4 for 5 hr at 90°C.

Weight loss (%)	Percent leached			
	U	Al	Fe	Ti
31	28	31	53	18
24	36	30	50	13

2.5 Acid Leaching

2.5.1 Single-stage leaching

Kingston fly ash was leached with various concentrations of HCl , HNO_3 , and H_2SO_4 at 20% solids for 72 hr on a Burrell shaker at ambient temperatures (20 to 24°C). Leach data for these tests, shown in Table 6, indicate relatively low metal recoveries: generally <15% for aluminum, <60% for iron, <35% for uranium, and <17% for titanium. These data indicate that direct leaching at ambient temperatures is not a satisfactory method for recovering metal values from fly ash.

Leaching of Kingston fly ash with the same three acids under reflux conditions provided moderate recoveries of uranium, iron, aluminum, and titanium. In these tests, the concentrations of the three acids were varied from 3 N to the concentrated reagent. A pulp density of 17% solids was maintained during the leaching period of 6 hr. Recoveries

Table 6. Leaching of Kingston fly ash with acids at ambient temperature

Leaching conditions: 72 hr at $\sim 20^{\circ}\text{C}$.

Acid	Acid conc. (N)	Wt loss (%)	Percent leached			
			U	Fe	Al	Ti
HCl	1.0	5.0	25	6	10	7
	3.0	8.0	27	13	12	9
	5.0	10.0	34	30	14	11
	8.0	14.0	34	52	15	16
	12.0	14.0	34	59	15	17
HNO ₃	1.0	6.0	21	5.9	8.5	7.8
	3.0	5.0	21	6.0	9.3	7.5
	5.0	7.0	24	6.3	9.9	8.1
	8.0	6.0	24	6.4	10.0	7.5
	12.0	4.0	14	5.7	7.2	3.6
	16.0	5.0	13	1.5	4.0	2.3
H ₂ SO ₄	1.0	6.0	23	5.7	9.1	7.9
	3.0	7.0	24	7.1	9.3	9.6
	5.0	6.0	24	9.3	10.2	9.3
	8.0	5.0	25	5.9	4.4	9.4
	12.0	5.0	24	7.2	3.8	9.8
	16.0	7.0	22	22.0	6.3	9.3
	36.0	8.0	21	34.2	5.4	8.5

are based on analyses of the air-dried leached residues. The data, listed in Table 7, indicate that maximum recoveries of iron and aluminum are achieved at an acid concentration of 8 N in each case.

A moderately high extraction of aluminum was achieved in three single-stage nitric acid leaches in which the pulp density was maintained at 10% solids. In these tests, either 8 N or 12 N HNO_3 was used as the leachant and the contact time was 24 to 48 hr at reflux temperature. The feed fly ash was the magnetically separated, low-iron fraction. Leaching data for aluminum, titanium, and iron, based on analyses of both the filtrate and residue, are shown in Table 8.

In preparation for aluminum recovery tests, an 8-liter batch of nitrate leach liquor was prepared by contacting 1500 g of fly ash with 8 liters of 8 N HNO_3 for 48 hr at 95°C. The leached solids were reslurried with 8 liters of H_2O and leached for 16 hr at 95°C. The total weight loss of the air-dried leached solids was 19%, and the aluminum recovery was 53%. Acid consumption for this leach was 15 meq of H^+ per gram of ash.

Similarly, an 8-liter batch of sulfate leach liquor was prepared by contacting 1500 g of fly ash with 8 liters of 8 N H_2SO_4 for 48 hr at 95°C. The leached solids were reslurried with 8 liters of H_2O and leached for 16 hr at 95°C. The total weight loss of the air-dried solids was 20%, and the aluminum recovery was 57%. Acid consumption for this leach was 2.6 meq of H^+ per gram of ash.

Leaching of Kingston fly ash under reflux conditions with a $\text{Ca}(\text{NO}_3)_2$ - HNO_3 mixture (10 N free HNO_3 , 16 N total NO_3^-) resulted in uranium, aluminum, iron, and titanium recoveries which were similar

Table 7. Leaching of Kingston fly ash with acids under reflux conditions

Leaching conditions: time, 6 hr; pulp density, 17% solids

Acid	Acid conc. (N)	Reflux temp. (°C)	Wt loss (%)	Percent leached			
				U	Fe	Al	Ti
HCl	3.0	100	16.4	28	77	46	22
	8.0	105	24.0	59	85	56	35
	12.0	108	20.2	64	84	53	35
HNO ₃	3.0	100	10.6	88	30	16	45
	8.0	105	17.6	95	56	57	48
	16.0	110	17.6	96	51	25	48
H ₂ SO ₄	3.0	100	14.6	56	54	43	28
	8.0	110	18.0	69	77	55	38
	16.0	135	16.6	65	69	42	43
	36.0	340	4.2	33	42	36	27

Table 8. Leaching of nonmagnetic fraction of Kingston fly ash with HNO₃ under reflux conditions

Leaching conditions: temperature, ~110°C; pulp density, 10% solids.

HNO ₃ conc. (N)	Time (hr)	% Al leached		% Ti leached		% Fe leached	
		Filtrate	Residue	Filtrate	Residue	Filtrate	Residue
8	24	56.9	54.6	29	30	57	50
8	48	69.7	63.4	32	37	37	33
12	48	71.3	62.0	22	38	33	41

to those obtained with 16 N free HNO_3 (somewhat lower than those obtained with 8 N free HNO_3).

In sulfuric acid pugging-type leaches, the addition of concentrated HCl actually reduced the amounts of uranium, aluminum, iron, and titanium leached from the ash. Results of the two pugging leaches are shown in Table 9. In these tests, concentrated H_2SO_4 was contacted with fly ash at a pulp density of 36%, heated to 90°C for 3 hr, diluted to 20% solids, and leached for an additional 3 hr. In one test, 10 ml of concentrated HCl was added to the 177 ml of H_2SO_4 before contacting the fly ash.

Table 9. Results obtained from H_2SO_4 pugging-type leaching of Kingston fly ash

Final H_2SO_4 conc. (<u>N</u>)	Final HCl conc. (<u>N</u>)	Wt loss (%)	Percent leached			
			U	Al	Fe	Ti
16	---	16.9	52	33	67	35
16	0.3	11.2	38	17	50	16

2.5.2 Multiple-stage leaching

A four-stage nitric acid leach of Kingston fly ash yielded only moderate recoveries of uranium, aluminum, and iron, and a low recovery of titanium. One sample of fly ash was calcined at 700°C for 3 hr and then leached in four stages of fresh 11 N HNO_3 at 66% solids for 3 hr each under reflux conditions. Leach stage recoveries, as well as the recovery based on the analysis of the leached solids, are shown in Table 10.

Table 10. Four-stage reflux leaching of
Kingston fly ash with HNO_3 solution

Leaching conditions: acid concentration,
11 N; pulp density, 66% solids; time,
3 hr per stage; temperature, $\sim 108^\circ\text{C}$.

Sample	Wt loss (%)	Percent leached			
		U	Al	Fe	Ti
Leach -1	---	25.4	20.8	12.9	2.0
-2	---	15.0	15.0	13.4	4.6
-3	---	7.9	7.3	13.2	3.7
-4	---	4.0	3.7	9.3	2.2
Total		52.3	46.8	48.8	12.5
Residue analysis	20	39.0	44.4	50.0	16.7

A second multiple-stage leach of fly ash with 8 N HNO_3 , which was made at 17% pulp density under reflux conditions, gave slightly higher metal recoveries than the four-stage leach at 66% pulp density. Table 11 shows the recoveries of aluminum after three stages of leaching for 5 hr per stage. Also included is the aluminum recovery based on the analysis of the residue.

A third multiple-stage leach of fly ash, which was made at 5% pulp density under reflux conditions, gave even higher metal recoveries than those at the higher pulp densities. Recoveries of aluminum after three stages of leaching for 5 hr per stage are shown in Table 12. Aluminum recovery, based on the analysis of the residue, is also included.

Table 11. Recovery of aluminum in a three-stage reflux leach of Kingston fly ash with HNO_3 solution

Leaching conditions: acid concentration, 8 N; pulp density, 17% solids; time, 5 hr per stage; temperature, 105°C.

Sample	Weight loss (%)	Percent of total Al leached
Leach -1	---	31.4
-2	---	5.1
-3	---	3.5 ($\Sigma = 40$)
Residue analysis	24.6	58.8

Table 12. Recovery of aluminum in a three-stage reflux leach of Kingston fly ash with HNO_3 solution

Leaching conditions: acid concentration, 8 N; pulp density, 5% solids; time, 24 hr per stage; temperature, 105°C.

Sample	Weight loss (%)	Percent of total Al leached
Leach -1	---	42.6
-2	---	5.8
-3	---	2.8 ($\Sigma = 51.2$)
Residue analysis	27.2	65.0

2.6 Extraction Tests

2.6.1 Extraction of metals from nitric acid leach liquors

Conceptual flowsheets for the recovery of aluminum from nitric acid leach liquors (described in detail in Sect. 2.5.1) suggest that iron be removed by solvent extraction prior to aluminum recovery. An added bonus in this extraction would be the recovery of uranium and titanium. Extraction tests were made on both direct leach solutions and secondary nitric acid leach solutions obtained after $\text{NaCl-Na}_2\text{CO}_3$ sintering and H_2O leaching of fly ash. Five-stage cascade extractions were made with 50 wt/vol % di-(2-ethylhexyl) phosphoric acid¹³ (HDEHP) in diethylbenzene (DEB) at a feed ratio of 1(org.):5(aq.). The aqueous feed solutions were pretreated by evaporation or addition of CaO for the reduction of free acid concentration. The recoveries of iron and titanium were high, while those of uranium and thorium were moderate to high. Essentially all of the extraction of these metals took place in the first two stages. In no case was any aluminum found to be extracted. Data for total metal recoveries, along with the source and pretreatment of the aqueous feeds used in the tests, are presented in Table 13. An overall flowsheet of the sequence of operations is shown in Fig. 10. A cost estimate of this process is given in Appendix C, along with the material balance flowsheets (Figs. C-1 through C-8) on which the estimate is based.

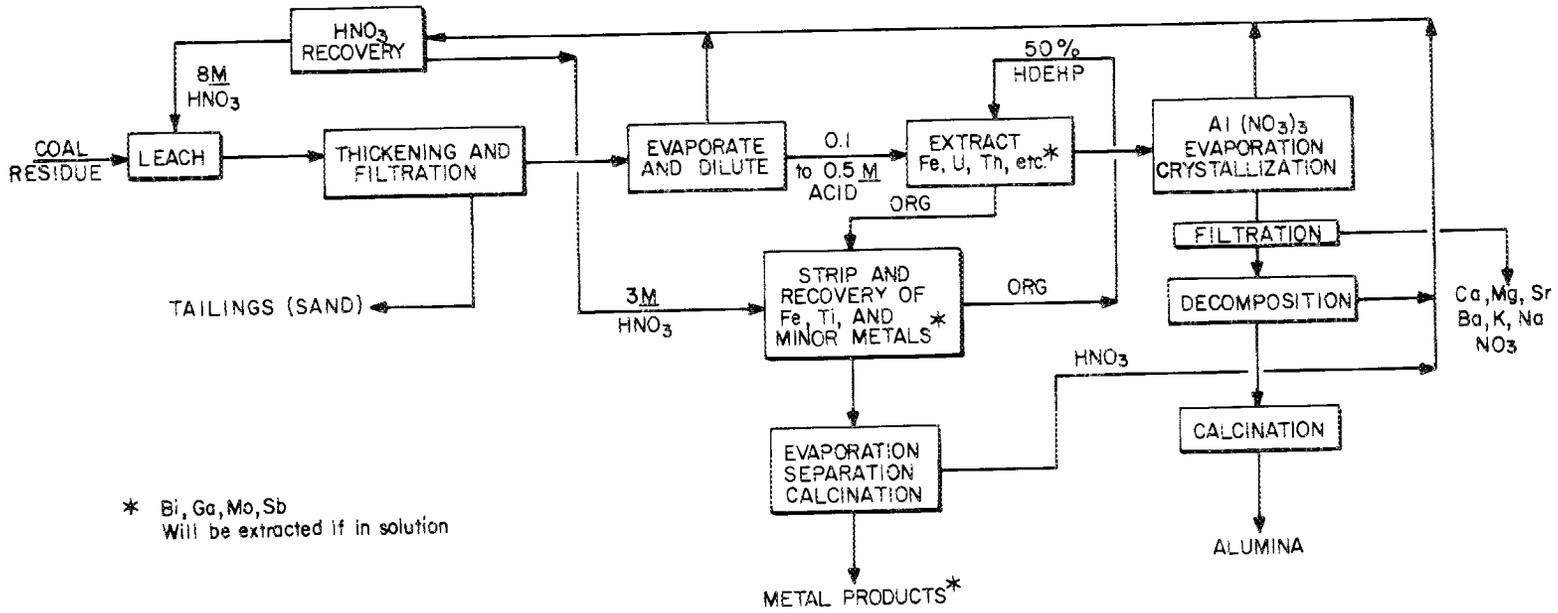
2.6.2 Extraction of metals from sulfuric acid leach liquors

Removal of iron as a preliminary step is also expedient in the recovery of aluminum from sulfuric acid leach liquors. The extractant chosen for effective extraction of iron from these sulfate liquors was

Table 13. Extraction of metals from HNO₃ leach liquors

Organic phase: 50 wt % HDEHP in DEB; aqueous phase: described in table;
 feed ratios: 1(org.)/5(aq.); contact: five-stage cascade, 30 min/stage.

Source of aqueous phase	pH	Percent extracted			
		Fe	Ti	U	Th
Direct HNO ₃ leach of fly ash; evaporation-dilution	0.5	97	97	57	86
Direct HNO ₃ leach of fly ash; CaO added	1.0	100	99	72	27
HNO ₃ leach of H ₂ O-leached fly ash; sinter	1.0	100	100	98	28
HNO ₃ leach of H ₂ O-leached fly ash; sinter	1.0	100	100	95	95
Direct acid leach of fly ash; CaO added	1.0	100	99	99	66



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Fig. 10. Nitric acid leach flowsheet.

a long-chain primary amine, 30 wt/vol % Primene JM-T in DEB.¹⁴ Five-stage cascade extractions were made with this organic solution at a feed ratio of 1(org.)/5(aq.). Extraction tests were made with two of the aqueous feeds that had no pretreatment, while the third had a pH adjustment to 1.0 with NaOH. The extractions of iron, titanium, uranium, and thorium were all high at pH 1.4, but dropped at lower pH values. Data for total metal recoveries, along with the source of the aqueous feeds, are shown in Table 14.

3. ECONOMIC EVALUATION

Three of the processes examined in our investigations appear to have merit for processing fly ash. These are: lime-soda-sinter, salt-soda-sinter--nitric acid leach, and nitric acid leach. Schematic flowsheets of the three processes are shown in Figs. 7, 9, and 10; material balance flowsheets and details of the cost estimates are given in Appendixes A, B, and C. In order to make the three processes comparable, the bases of design were fixed as follows:

- (1) The plant capacity is 1×10^6 tons of fly ash (dry basis) per year as slurried product from the fossil-fueled plant collectors, containing 66 wt % water.
- (2) The fly ash to be processed is obtained from the TVA Kingston Steam Plant.
- (3) Removal of an iron-rich fraction by magnetic separation is the first step in each process.
- (4) The plant is located at the TVA Kingston Steam Plant site.

Table 14. Extraction of metals from H₂SO₄ leach liquors

Organic phase: 30 wt/vol % Primene JM-T in DEB; aqueous phase: listed in table;
 feed ratios: 1(org.)/5(aq.); contact: five-stage cascade, 30 min/stage.

Source of aqueous feed	pH	Percent extracted			
		Fe	Ti	U	Th
H ₂ SO ₄ leach of H ₂ O-leached sinter	1.4	100	99	98	75
Direct H ₂ SO ₄ leach of fly ash + NaOH	1.0	79	97	20	89
Direct H ₂ SO ₄ leach of fly ash; no adjustment	---	66	94	19	72

Summaries of the cost estimates of three of the processes investigated are given in Table 15. Since the flowsheets on which the cost estimates were based are conceptual, the costs should be considered preliminary. This type of estimate prepared from a flowsheet and a minimum of equipment data can be expected to be fairly inaccurate (i.e., within 30% of the actual cost). However, such estimates can be used legitimately to make a comparison of processes because the evaluation methods are identical in each case. Results of the comparison showed reasonable agreement in the costs of the plants; however, the operating costs were significantly different. The income from products for the lime-soda-sinter and salt-soda-sinter processes is high because of the large quantities of cement and silica gel produced. A market for such amounts of product would need to be found before these profits could be considered realistic. The uncertainty arises from the fact that pricing of a product depends on form, purity, and suitability as input to other processes. The quantities of ash consumed for the lime-soda-sinter, salt-soda-sinter--nitric acid leach, and nitric acid leach processes are 90, 60, and 30%, respectively. From a total ash usage viewpoint, the lime-soda-sinter has considerable merit, provided a market can be found for the cement produced.

4. SUMMARY AND CONCLUSIONS

It is concluded from our studies that additional research is necessary to determine the optimum method for processing fly ash for recovery of resource materials. Evaluation of the economic and technical factors indicates no significant differences in the three processes for which

Table 15. Summary of cost estimates for recovery
of resource materials from fly ash

1×10^6 tons/year (dry basis)

Process	Cost of plant ^a (\$)	Annual operating cost (\$)	Income from products (\$)
Lime-soda-sinter	61,892,000	43,393,055	119,542,975
Salt-soda sinter-- nitric acid leach	58,006,000	32,461,475	109,191,573
Nitric acid leach	66,316,000	22,448,150	31,114,425

^aIf land and utilities are not available, add 30% to plant costs.

cost estimates were prepared; however, a study of the marketability of the products and a detailed estimate of the costs to produce them would probably show which of the processes is the most desirable. The salt-soda-sinter--nitric acid leach process has merit over the lime-soda-sinter method in that it is adaptable to the recovery of a number of materials; however, it is a more corrosive process. The nitric acid leach process appears to be the least desirable because of the lower percentages of extractable products and lower consumption of fly ash when compared with the other two processes. In the final analysis, the most economical process may be one that combines disposal or environmental credits with product value to help "pay its way."

From the data obtained to date, we have identified the following areas of research which require additional development. These steps in the various processes will first need to be ordered according to the importance of their economic and technical aspects.

1. Process step to remove cenospheres, which are fly-ash particles that float; such material is useful¹⁵ and has a potential value of \$100/ton. The quantity in the TVA Kingston fly ash is ~ 1 wt %.
2. Equipment to optimize the removal and concentration of magnetic iron and development of a separation technique that reduces the quantity of potassium in the magnetic iron fraction from the fly ash. If unsuccessful, the total iron may be removed as high-grade iron in certain processes by special separation techniques.

3. Lime-soda-sinter process

- (a) Sintering -- $\text{CaO}/\text{Al}_2\text{O}_3$ and CaO/SiO_2 mole ratios, along with sintering temperature, reaction time, and rate of cooldown need to be optimized.
- (b) Leaching -- $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ mole ratio needs to be optimized.
- (c) Desilication -- temperature and pressure in this reaction need to be optimized.
- (d) Products of the lime-soda-sinter process, which go into cement, need to be varied and a study made of the materials that can be added to yield the type of cement in demand.

4. Salt-soda-sinter process

- (a) Obtain more information to determine whether HNO_3 or H_2SO_4 should be the leachant.
- (b) Investigate the possibility that AlCl_3 might be volatilized during sintering with $\text{NaCl}-\text{Na}_2\text{CO}_3$ mixtures.
- (c) Determine the feasibility of removing iron from HNO_3 leach solutions by evaporation and controlled hydrolysis. This possibility should be pursued as an economic alternative to solvent extraction.
- (d) Develop steps to maximize the recovery of HNO_3 or H_2SO_4 .
- (e) Test new sintering mixtures of the sulfate, chloride, and carbonate salts of calcium, potassium, and sodium.

- (f) Investigate the possibility of leaching sintered material at controlled pH or reducing the acidity in a controlled manner in the leachate so as to either leave iron undissolved in the residue or selectively precipitate iron hydroxide.
 - (g) Examine the effect of all treatments above on the microscopic structure of fly ash.
5. Study of factors associated with filtration difficulties encountered in direct acid leaching, as well as in secondary acid leaching following salt-soda sintering and water-leaching of fly ash. Large-area filtration equipment would be required for efficient solids-liquid separation. In general, any method which would require filtration of this type of material would demand a thorough investigation in order to determine the most efficient type of equipment and optimum operating conditions.
 6. Economic analysis of product value vs purity from the various treatment processes being considered to determine realistic costs due to losses of solvents and acids for the various processes.

5. ACKNOWLEDGMENTS

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Special thanks go to K. D. Cook, of the ORNL Engineering Division, for preparing the cost estimates based on the three conceptual flowsheets.

We also wish to express our appreciation to Kevin Felker, Warren Sisson, David Sellinger, and Mildred McClure, who performed much of the laboratory experimental work.

6. APPENDIXES

6.1 Appendix A: Cost Analysis and Material Balance for the Lime-Soda-Sinter Process

A cost estimate of a lime-soda-sinter process to produce iron oxide, alumina, and cement from 1×10^6 tons of fly ash per year (dry basis) is summarized below. All costs are given in 1977 dollars.

Total facility cost	\$61,892,000 ^a
Total operating costs	\$43 x 10 ⁶
Income from sale of products	\$119 x 10 ⁶

^aAdd 30% if land and utilities are required.

The various costs are detailed in Tables A-1 through A-4. Material balances are shown in Figs. A-1 through A-10.

Table A-1. Breakdown of facility cost

Magnetic Fly Ash Facility	
Construction	\$2,009,000
Engineering	502,000
Contingency	<u>1,256,000</u>
Total	\$3,767,000
Nonmagnetic Fly Ash Facility	
Construction	\$31,000,000
Engineering	7,750,000
Contingency	<u>19,375,000</u>
Total	\$58,125,000

Table A-2. Operating costs of lime-soda-sinter process

Limestone	4476 tons/day x 365 days/year x \$6/ton	\$ 9,802,440
Soda ash	225 tons/day x 365 days/year x \$105/ton	9,772,875
Natural gas	1,200,000 ft ³ /hr x 24 hr/day x 365 days/year x \$0.001/ft ³	10,512,000
Solvent extractant (est.)	55 tons/day x 365 days/year x \$188/ton	3,774,100
Gypsum	106 tons/day x 365 days/year x \$36/ton	1,392,840
Electrical power	6000 kW (24 hr/day)(365 days/year x \$0.015/kWhr)	788,400
Steam	20,000 lb/hr (24 hr/day)(365 days/ year)(\$0.002/lb)	350,400
Operating labor	10 at \$25,000 x 4 shifts	1,000,000
Maintenance	10% initial cost	<u>6,000,000</u>
		Total \$43,393,055

Table A-3. Income from products of
lime-soda-sinter process

Iron pellets	300 tons/day x 365 days/year x \$30/ton	\$ 3,285,000
Alumina	571 tons/day x 365 days/year x \$155/ton	32,304,325
Cement	4182 tons/day x 365 days/year x \$55/ton	<u>83,953,650</u>
		\$119,542,975

Table A-4. Equipment cost summary

Item	Cost (\$)	
	Material	Labor
<u>Magnetic Separation System</u>		
Slurry pipe	180,000	14,400
Pumps	18,000	1,152
Magnetic separator, three stage	180,000	4,860
Clarifier, thickeners	65,000	8,280
Dryer, steam heated	100,000	3,150
Solvent extractor contactor	180,000	8,100
Recycle pumps	15,600	1,296
Solvent storage tanks	255,000	a
Injector pumps, 0 to 60 gpm	10,500	432
Unloading pumps, 900 gpm	9,000	432
Screw feeder	3,900	324
Cone pelletizer	65,000	288
Binder injector, spray unit	5,000	216
Tunnel dryer	30,000	1,440
Pellet hopper	60,000	a
Structures and foundations	43,500	13,500
Electrical	8,000	8,100
Piping-steam-gas-process	15,000	9,000
Instrumentation	21,000	13,500
Miscellaneous	126,500	8,830
	LSPC ^b direct....\$1,391,000	\$97,300
	Overhead + administration.....	520,700
	LSPC ^b total.....	2,009,000
<u>Nonmagnetic System</u>		
A. Sinter		
Clarifier thickener	133,400	14,400
Limestone conveyor	28,000	3,600
Primary crusher	147,928	4,068
Pulverizer	750,000	10,800
Limestone storage silo	260,000	a
Screw feeder	8,000	648
Ejector-water	8,200	576
Mixer	30,400	1,152
Pneumatic unloader conveyor for soda ash	90,000	10,800
Storage silo for soda ash	65,000	a

^aFabricated in place.

^bLump-sum prime contract.

Table A-4. (continued)

Item	Cost (\$)	
	Material	Labor
Ejector	8,200	576
Mixer	30,400	1,161
Tank, soda ash solution	72,000	a
Pumps	5,340	324
Storage tanks, desilicated residue	60,000	a
Pumps	10,500	432
Wet grinder, rotary drum type	380,000	13,500
Vibrating separator	40,250	1,080
Sintering kilns	1,125,000	54,000
Sinter feeder belt conveyor	105,000	4,500
B. Leaching		
Leaching tanks	200,000	a
Pumps - 750 gpm	15,600	1,890
Pumps - 500 gpm	12,600	1,620
Storage tanks, leaching solution	144,000	a
Thickeners	575,700	67,500
Wash tanks	130,000	a
Wash pumps	17,800	2,700
Backwash filters	212,000	4,320
Backwash pumps	23,310	2,025
Makeup pumps	6,964	810
Tailings pump	72,500	2,025
Tailings pumpline	70,000	2,160
C. Desilication		
Feed pumps	36,000	1,215
Limestone conveyor	21,000	3,780
Rotary kiln	68,000	8,100
Lime slaking tanks	59,390	1,350
Autoclaves	252,000	13,500
Flash tanks	72,900	4,860
Settling tanks	126,000	8,100
Pumps	26,000	1,620
Residue filters	23,100	1,296
Residue pumps	11,200	810
D. Carbonization		
Screw drum heater	928,000	72,000
Hydroclassifier	152,000	10,800
Thickener	225,000	19,800

^aFabricated in place.

Table A-4. (continued)

Item	Cost (\$)	
	Material	Labor
Recycle pump	7,036	810
Mechanical classifier	16,100	432
Filter	67,600	2,880
Pumps - 500 gpm	7,036	810
Pumps - 400 gpm	13,000	810
Filtrate pumps	13,000	8,100
E. Calcination		
Evaporator	16,000	1,620
Calcining kilns	530,000	27,000
Pulverizer	24,000	288
Automatic bagging scale	18,000	270
F. Soda Ash Recovery		
Evaporator	26,000	2,160
Mixing tank	26,000	a
Pumps - 500 gpm	7,036	810
Pumps - 600 gpm	9,400	810
G. Flue Gas Processing		
Scrubber	119,000	1,152
Blower	32,000	1,440
Pumps	24,000	810
Compressor	18,000	1,440
H. Cement Process		
Rotary kilns	2,650,000	162,000
Pulverizer	56,000	5,760
Rotary auger blender	34,000	864
Automatic bagging scale	72,000	1,080
Gypsum storage and feeder	76,000	a
Cement bag palletizer	52,000	8,640
Structures and foundations	860,000	148,500
Electrical	500,000	135,000
Piping - steam-gas-process	900,000	162,000
Instrumentation	3,200,000	180,000
Control room building and warehouses	2,400,000	1,512,000
Plant air compressor	129,000	1,872

^aFabricated in place.

Table A-4. (continued)

Item	Cost (\$)	
	Material	Labor
Instrument air dryer	9,500	1,440
Miscellaneous	937,610	287,941
LSPC ^b direct.....	\$19,688,000	\$3,164,000
Overhead + administration.....	\$ 8,148,000	
LSPC ^b total.....	\$31,000,000	

^aFabricated in place.

^bLump-sum prime contract.

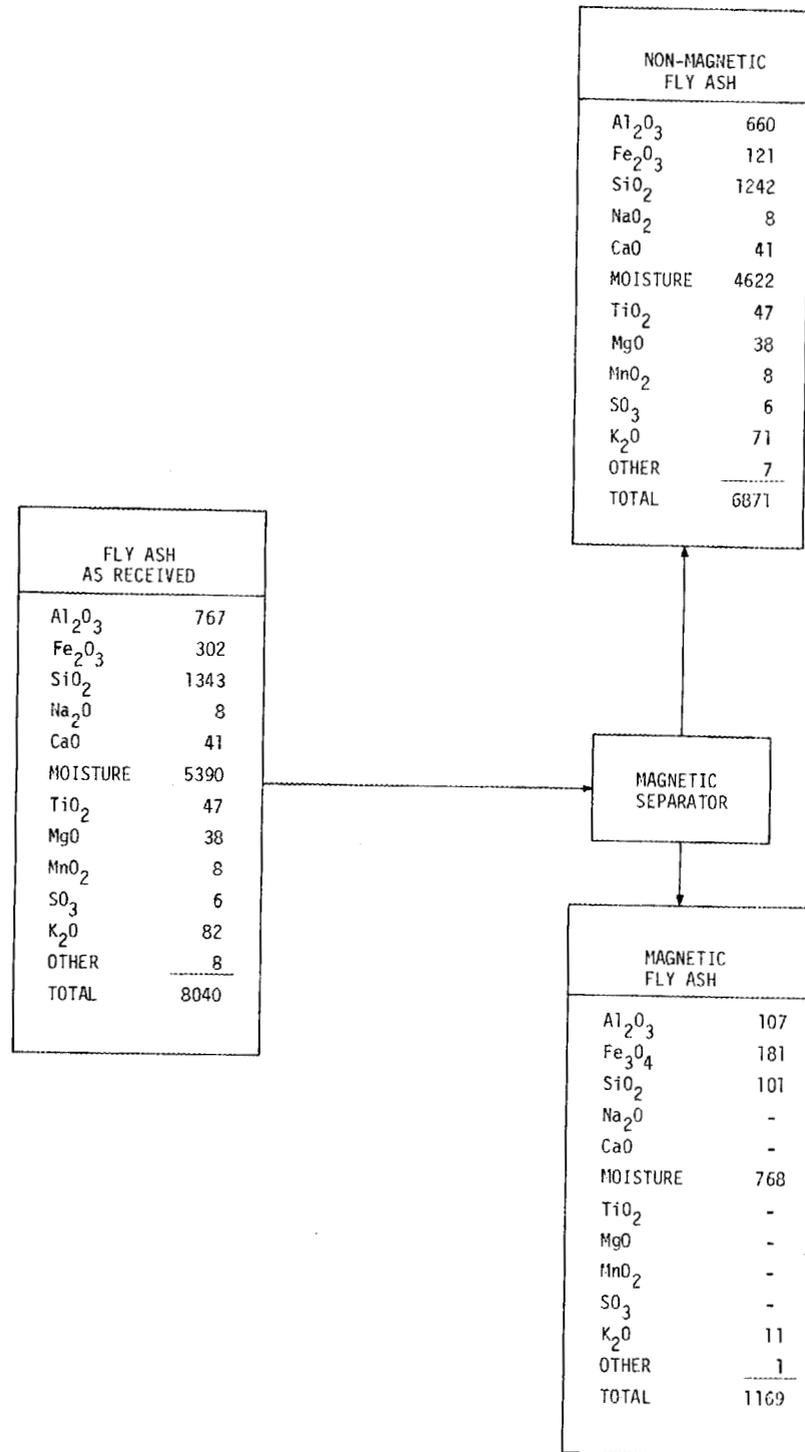


Fig. A-1. Material balance for magnetic separator section, lime-soda-sinter process (tons/day).

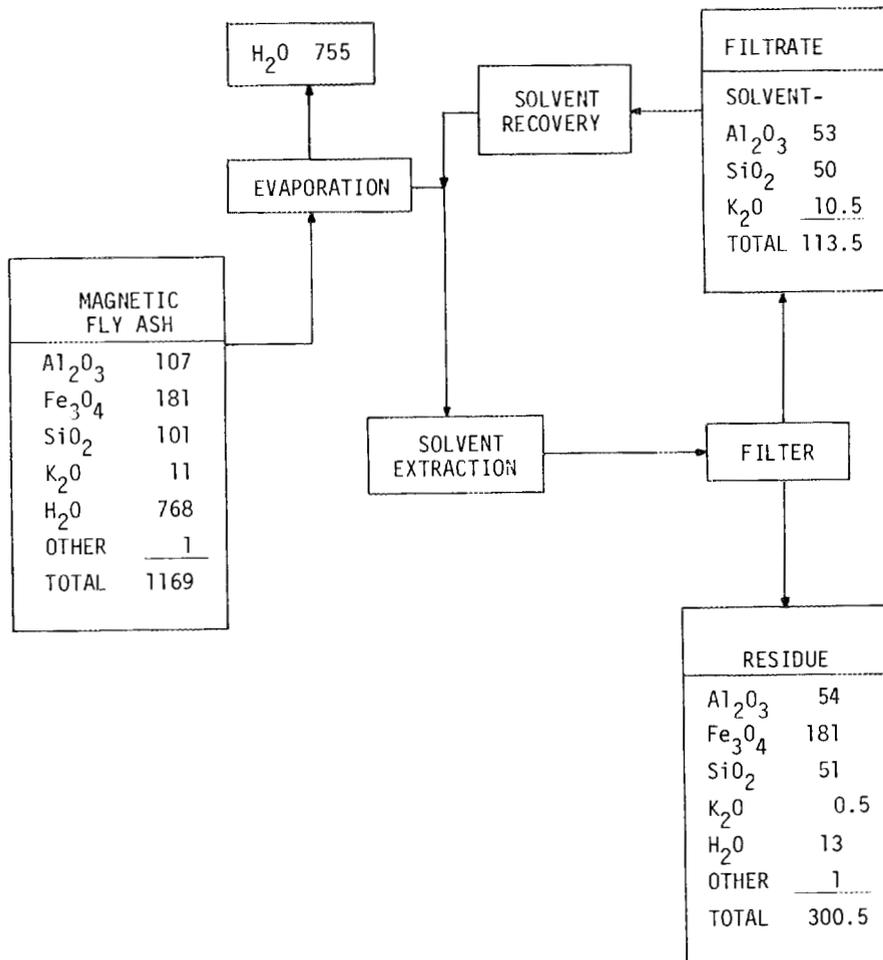


Fig. A-2. Material balance for magnetic iron purification section, lime-soda-sinter process (tons/day).

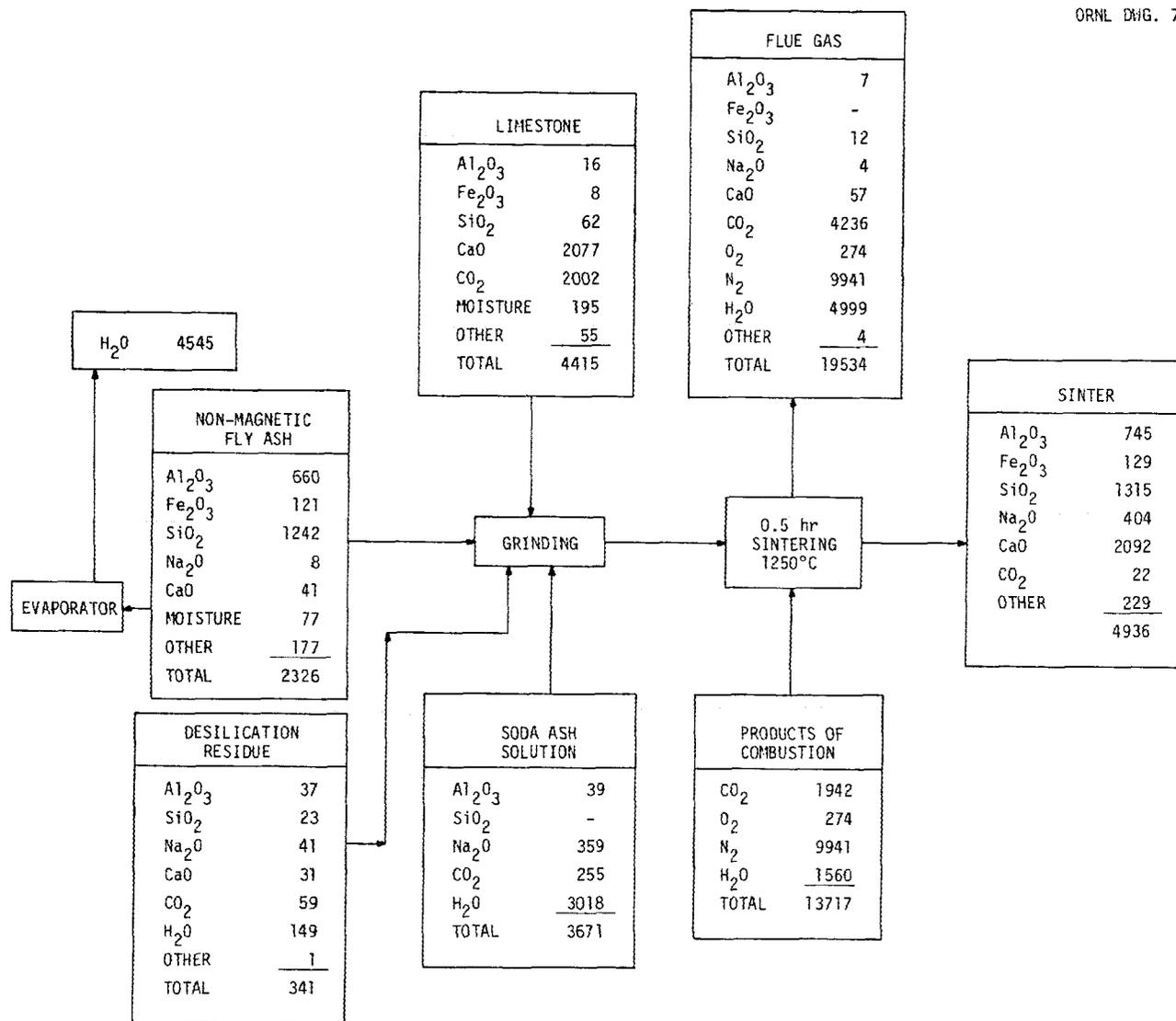


Fig. A-3. Material balance for sintering section, lime-soda-sinter process (tons/day).

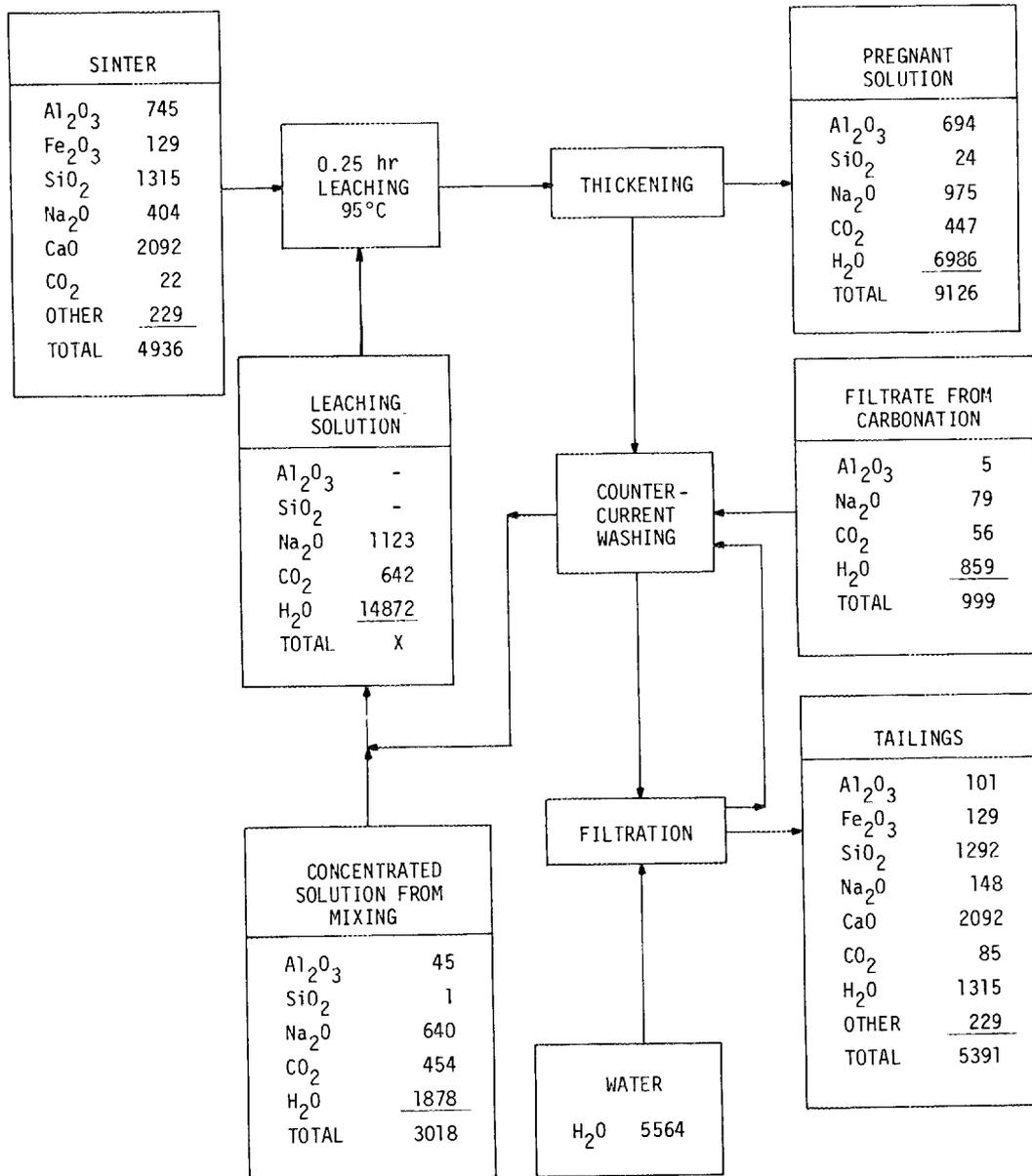


Fig. A-4. Material balance for leaching section, lime-soda-sinter process (tons/day).

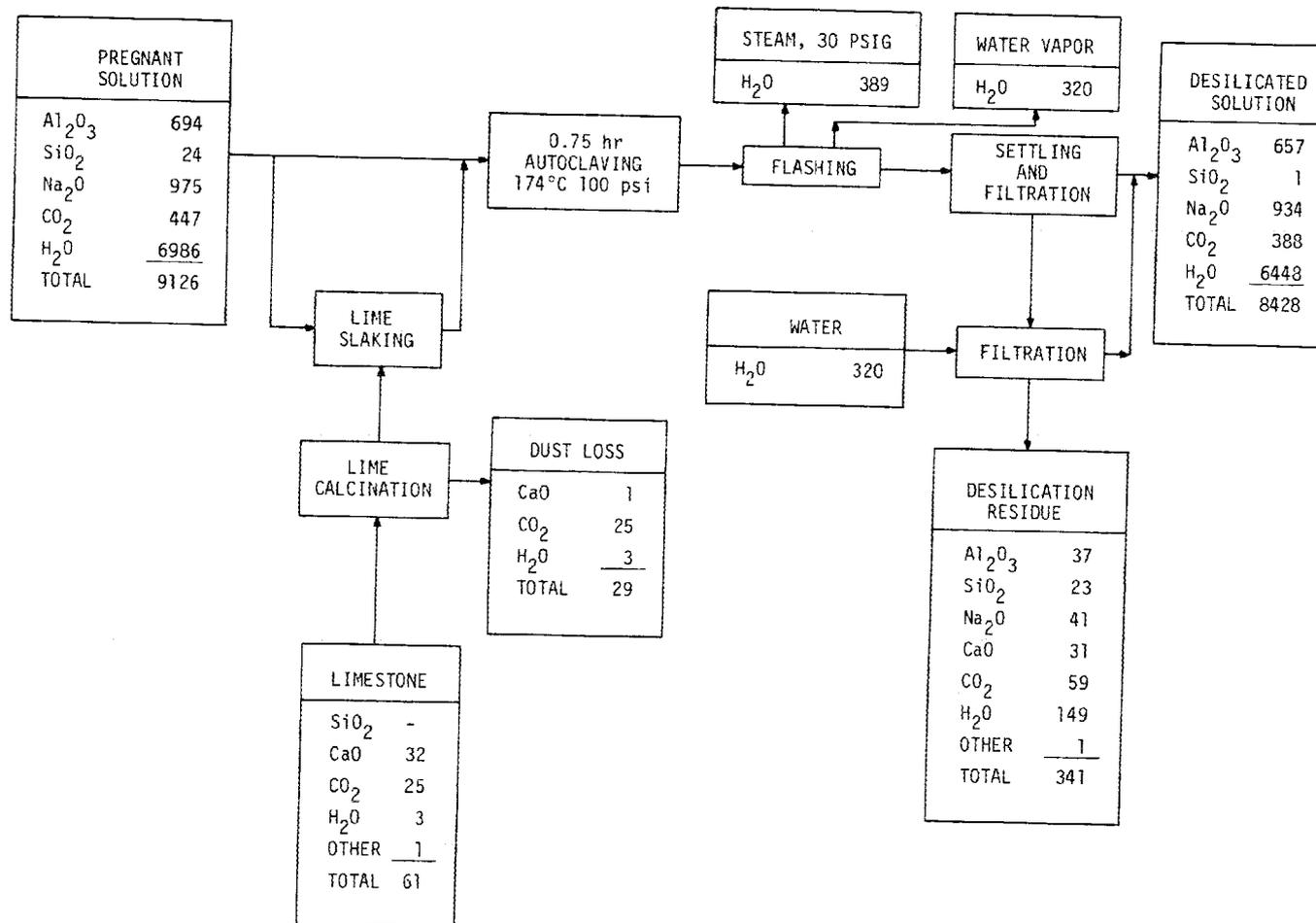


Fig. A-5. Material balance for desilication section, lime-soda-sinter process (tons/day).

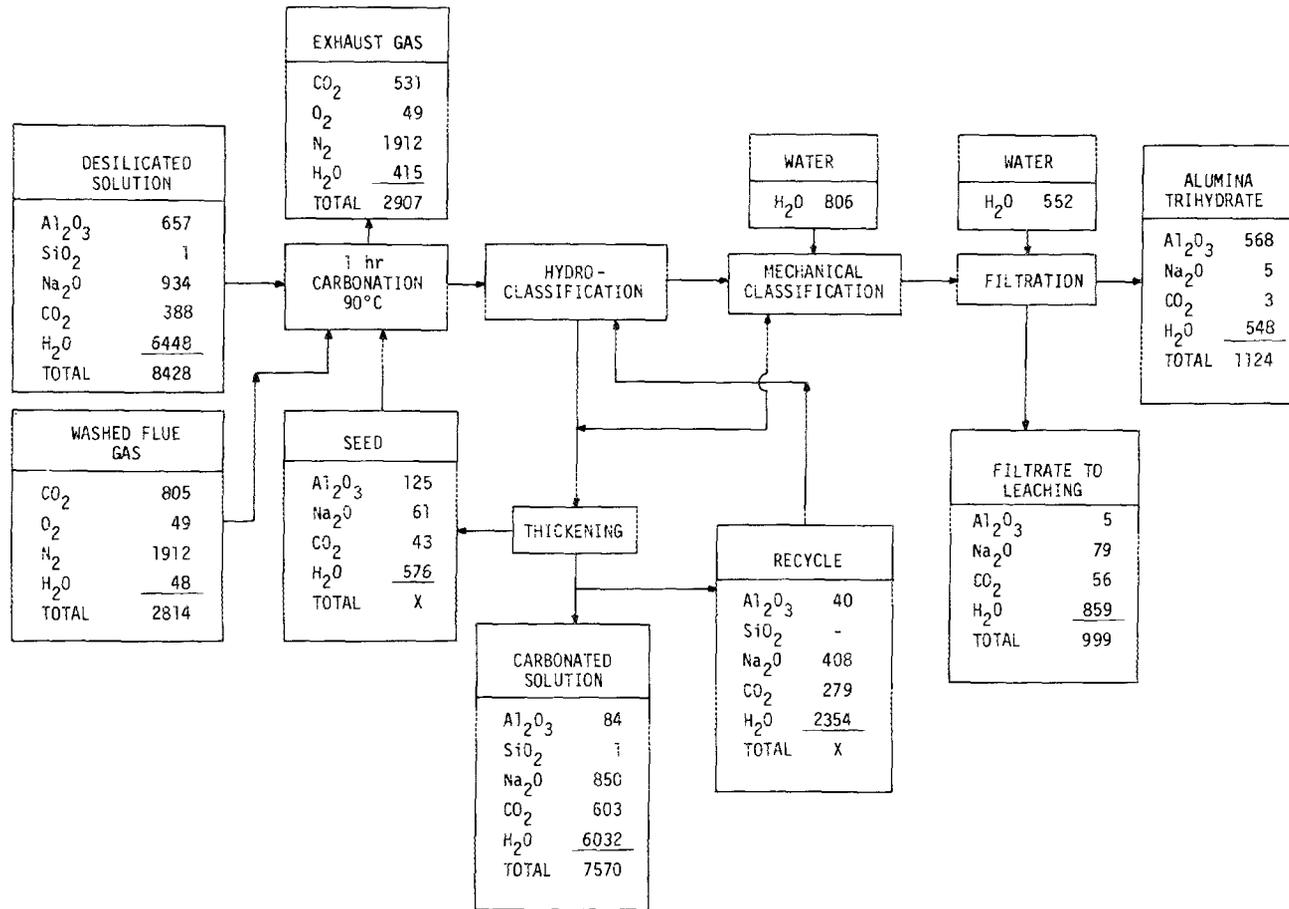


Fig. A-6. Material balance for carbonation section, lime-soda-sinter process (tons/day).

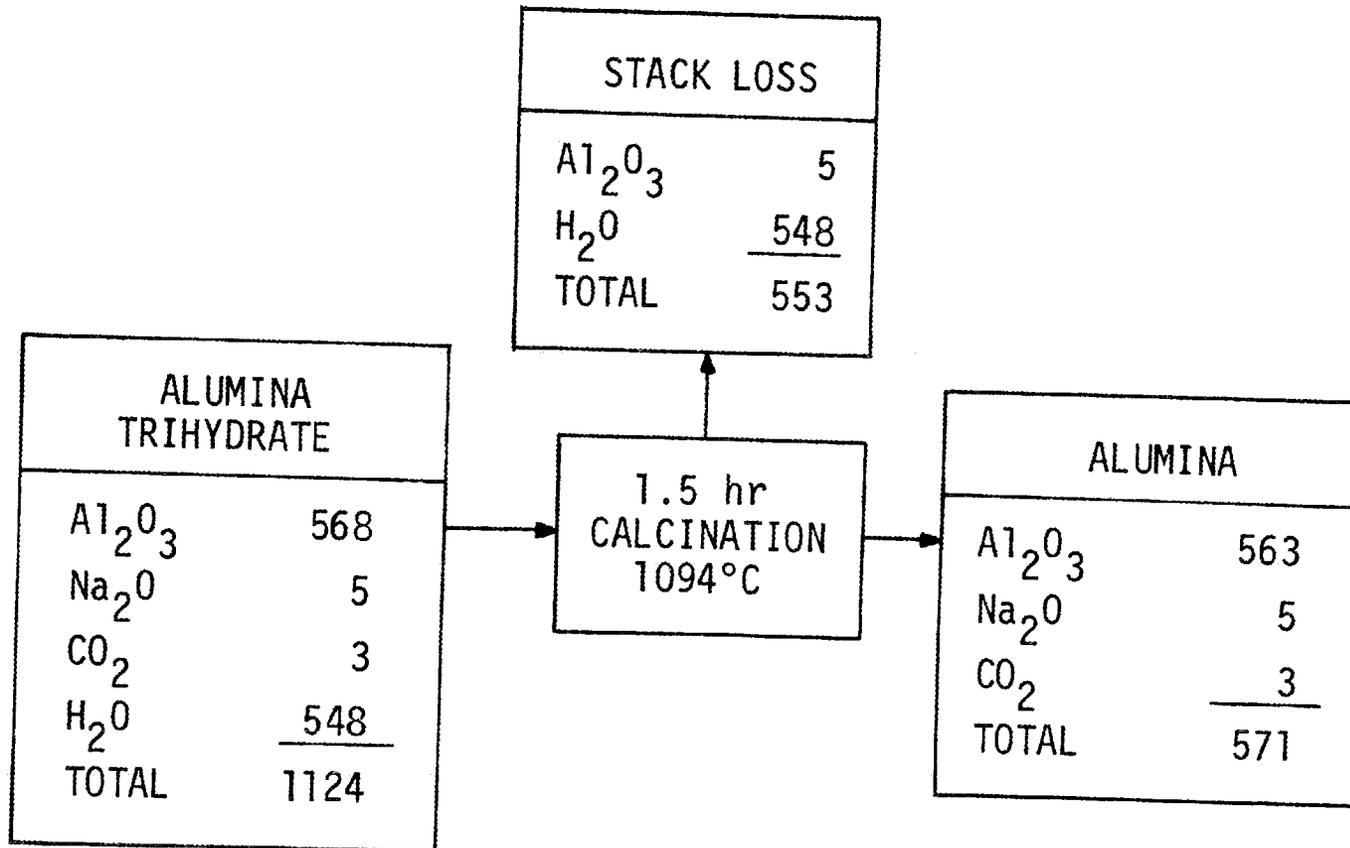


Fig. A-7. Material balance for calcination section, lime-soda-sinter process (tons/day).

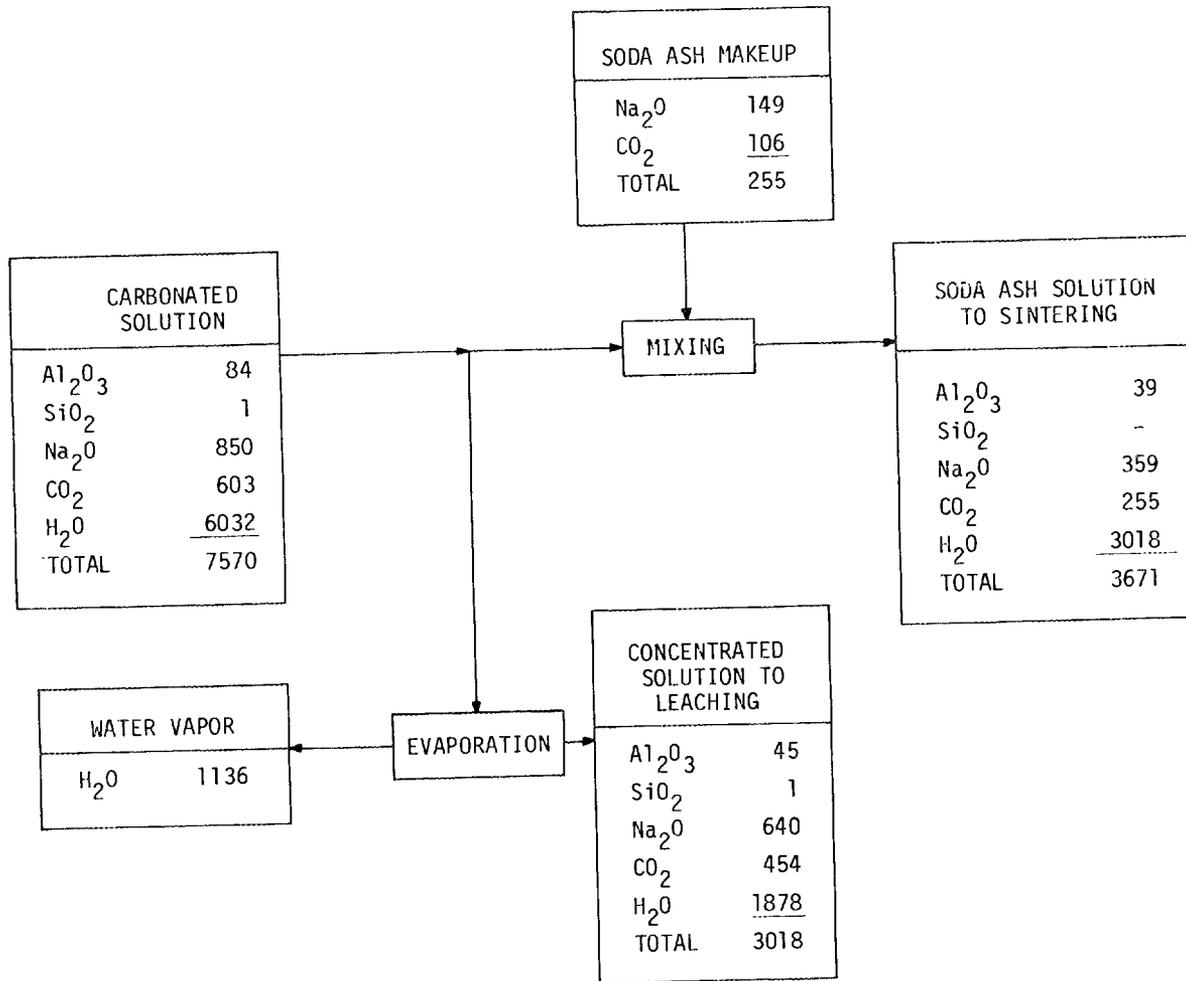


Fig. A-8. Material balance for soda ash recovery section, lime-soda-sinter process (tons/day).

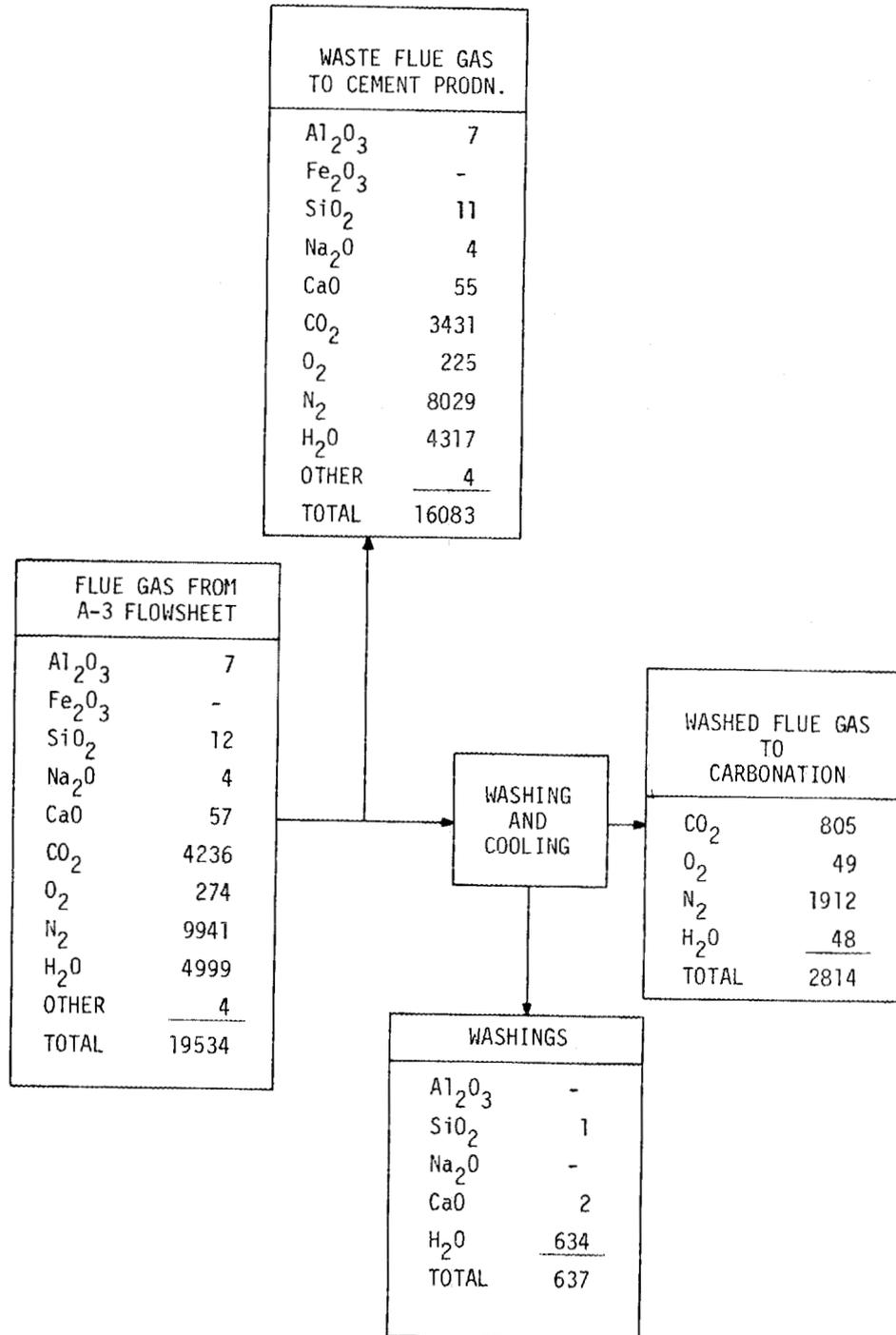


Fig. A-9. Material balance for flue gas processing section, lime-soda-sinter process (tons/day).

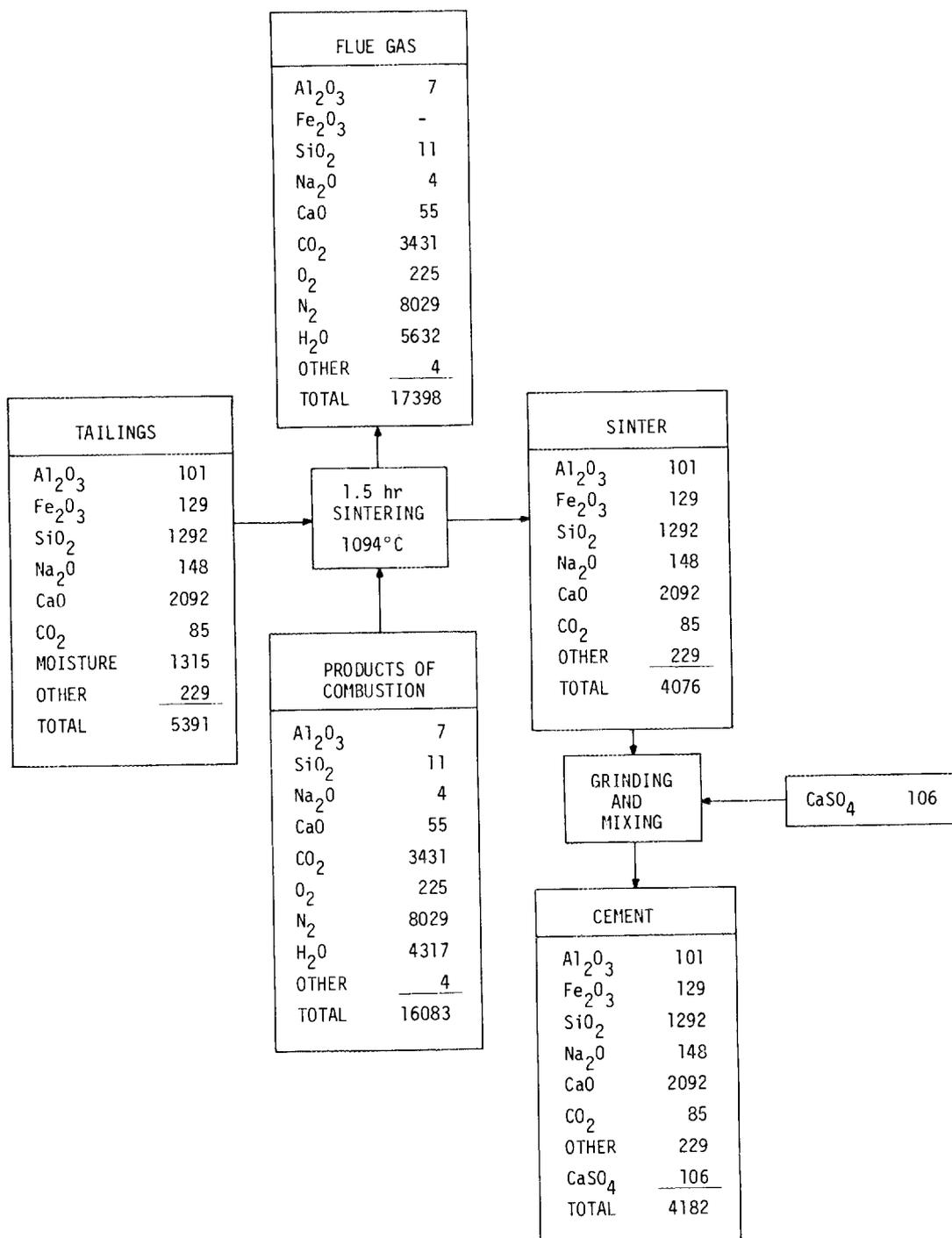


Fig. A-10. Material balance for the sinter for production of cement, lime-soda-sinter process (tons/day).

6.2 Appendix B: Cost Analysis and Material Balance for the
Salt-Soda-Sinter--Nitric Acid Leach Process

A cost estimate of a salt-soda-sinter--nitric acid leach process to produce iron oxide, alumina, manganese dioxide, titanium dioxide, and silica gel from 1×10^6 tons of fly ash per year (dry basis) is summarized below. All costs are in 1977 dollars.

Total facility cost	\$ 66,316,000 ^a
Total operating costs	\$ 32,462,125
Income from products	\$109,191,573

^aAdd 30% if land and utilities are required.

The various costs are detailed in Tables B-1 through B-4. Material balances are shown in Figs. B-1 through B-9.

Table B-1. Breakdown of facility cost

Magnetic Separation Section	
Construction	\$2,009,000
Engineering	502,000
Contingency	<u>1,256,000</u>
Total	\$3,767,000
Salt-Soda-Sinter Section	
Construction	\$12,800,000
Engineering	3,200,000
Contingency	<u>8,000,000</u>
Total	\$24,000,000
Nitric Acid Leach Section	
Construction	\$20,559,000
Engineering	5,140,000
Contingency	<u>12,850,000</u>
Total	\$38,549,000

Table B-2. Operating costs of salt-soda-sinter--nitric acid leach process

Soda ash	225 tons/day x 365 days/year x \$105/ton	\$ 8,623,125
Solvent extractant (est.)	55 tons/day x 365 days/year x \$188/ton	4,204,800
Salt	450 tons/day x 365 days/year x \$14/ton	2,299,500
HDEHP	2 tons/day x 365 days/year x \$3700/ton	2,701,000
Kerosene	1.5 tons/day x 365 days/year x \$100/ton	54,750
Nitric acid	4 tons/day x 365 days/year x \$375/ton	547,500
Electric power	(6000 kW) (24 hr/day) (365 days/year) (\$0.015/kWhr)	788,400
Steam	20,000 lb/hr (24 hr/day) (365 days/year) (\$0.002/lb)	350,400
Natural gas	600,000 ft ³ (24 hr/day) (365 days/year) (\$0.001/ft ³)	5,256,000
Operating labor	10 at \$25,000 x 4 shifts	1,000,000
Maintenance	10% initial cost	<u>6,636,000</u>
		\$32,461,475

Table B-3. Income from sale of products

Iron pellets	300 tons/day x 365 days/year x \$30/ton	\$ 3,285,000
Alumina	594 tons/day x 365 days/year x \$155/ton	33,605,550
Iron	109 tons/day x 365 days/year x \$5/ton	198,925
MnO ₂	7 tons/day x 365 days/year x \$200/ton	511,000
TiO ₂	42 tons/day x 365 days/year x \$530/ton	8,124,900
Silica gel	621 tons/day x 365 days/year x \$280/ton	<u>63,466,200</u>
		\$109,191,575

Table B-4. Equipment cost summary

Item	Cost (\$)	
	Material	Labor
<u>Magnetic Separation System</u>		
Slurry pipe	180,000	14,400
Pumps	18,000	1,152
Magnetic separator, three-stage	180,000	4,860
Clarifier, thickeners	65,000	8,280
Dryer, steam heated	100,000	3,150
Solvent extractor contactor	180,000	8,100
Recycle pumps	15,600	1,296
Solvent storage tanks	255,000	a
Injector pumps, 0 to 60 gpm	10,500	432
Unloading pumps, 900 gpm	9,000	432
Screw feeder	3,900	324
Cone pelletizer	65,000	288
Binder injector, spray unit	5,000	216
Tunnel dryer	30,000	1,440
Pellet hopper	60,000	a
Structures and foundations	43,500	13,500
Electrical	8,000	8,100
Piping-steam-gas-process	15,000	9,000
Instrumentation	21,000	13,500
Miscellaneous	126,500	8,830
	LSPC ^b direct....\$1,391,000	\$97,300
	Overhead + administration..... 520,700	
	LSPC total..... 2,009,000	
<u>Nonmagnetic System</u>		
A. Sinter		
Thickener	133,400	14,400
Conveyor	85,000	9,000
Salt storage	160,000	a
Salt feeder	4,800	288
Soda conveyor	85,000	9,000
Soda storage	90,000	a
Fly-ash feeder	78,000	2,160
Blender	150,000	4,320
Rotary kilns	2,600,000	108,000
Sinter cooler	260,000	9,000
Sinter feeders	24,600	2,160
Grinders	408,000	16,200

^aFabricated in place.

^bLump-sum prime contract.

Table B-4. (continued)

Item	Cost (\$)	
	Material	Labor
Leaching tanks	360,000	216,000
Slurry pumps	140,000	6,480
Leach pumps	40,500	2,835
Filters	57,000	1,296
Slurry feeders	72,000	2,160
Evaporators	532,000	18,000
Recycle feeders	24,000	1,440
Structures and foundations	530,000	351,000
Electrical	265,000	177,300
Piping-steam-gas	300,000	199,800
Instrumentation	750,000	321,300
Miscellaneous	715,300	146,761
	LSPC direct....\$7,865,000	\$1,618,000
	Overhead + administration.....\$ 3,317,000	
	LSPC total.....\$12,800,000	
Nitric Acid		
Acid storage tank	38,000	10,800
Acid pumps	7,000	900
Acid metering pumps	3,000	432
Mixers	27,000	1,620
Acid leach pumps	1,260,000	288,000
Leach pumps	84,000	2,160
CO ₂ blower and stack	150,000	5,580
Residue tanks	450,000	216,000
Residue dryer	540,000	16,200
Condensers	84,000	4,320
Recycle pumps	21,600	1,440
Residue conveyor	450,000	a
Filtrate pumps	32,000	2,160
HDEHP storage tanks	7,000	2,160
Organic pumps	4,600	288
Organic metering pumps	3,000	144
Kerosene storage tanks	7,000	2,160
Unloading pumps	4,600	288
Metering pumps	3,000	144
Mixing storage tanks	28,800	a
Separator tanks	36,000	155,200
Water transfer pumps	25,600	1,440
Organic transfer pumps	18,920	1,440
Evaporator	48,000	144,000

^aFabricated in place.

Table B-4. (continued)

Item	Cost (\$)	
	Material	Labor
Condenser	136,000	2,700
Acid pumps	2,400	1,440
Settling tanks	24,000	144,000
Drum flaker dryers	200,000	9,000
Weighing and bagging station	48,000	1,080
Evaporator	24,000	144,000
Condenser	136,000	2,700
Nitric acid pumps	24,000	1,440
Residue feeders	9,000	864
Blenders	15,200	576
Filter	16,200	432
Drum dryers	70,000	2,232
Rotary calciners	260,000	10,800
Conveyor and coolers	26,000	1,800
Weigh-hopper and car loader	48,000	4,320
Filtrate evaporator pumps	15,200	864
Evaporator-crystallizers	64,000	2,880
Oven feeders	9,000	2,664
Ovens	56,000	8,100
Conveyors	18,000	1,800
Weigh-hopper-car loaders	48,000	4,320
Condenser	52,000	2,160
Acid return pumps	18,000	864
Stripper tank	36,000	115,200
Recycle pumps	25,200	1,440
Water pumps	24,000	1,440
Evaporator	76,000	10,800
Condensers	6,000	10,800
Acid pumps	21,600	1,440
Nitric acid tanks	250,000	a
Rotary heater	9,800	1,440
Conveyor cooler	6,000	1,440
Weigh hopper and loader	12,000	2,070
Structures and foundations	494,000	198,000
Electrical	742,000	297,000
Piping-steam-gas	1,731,000	630,000
Instrumentation	1,483,000	441,000
Buildings	500,000	747,000
Miscellaneous	1,022,000	362,000
LSPC direct....	\$11,238,000	\$3,990,000
Overhead + administration.....	\$ 5,331,000	
LSPC total.....	\$20,559,000	

^aFabricated in place.

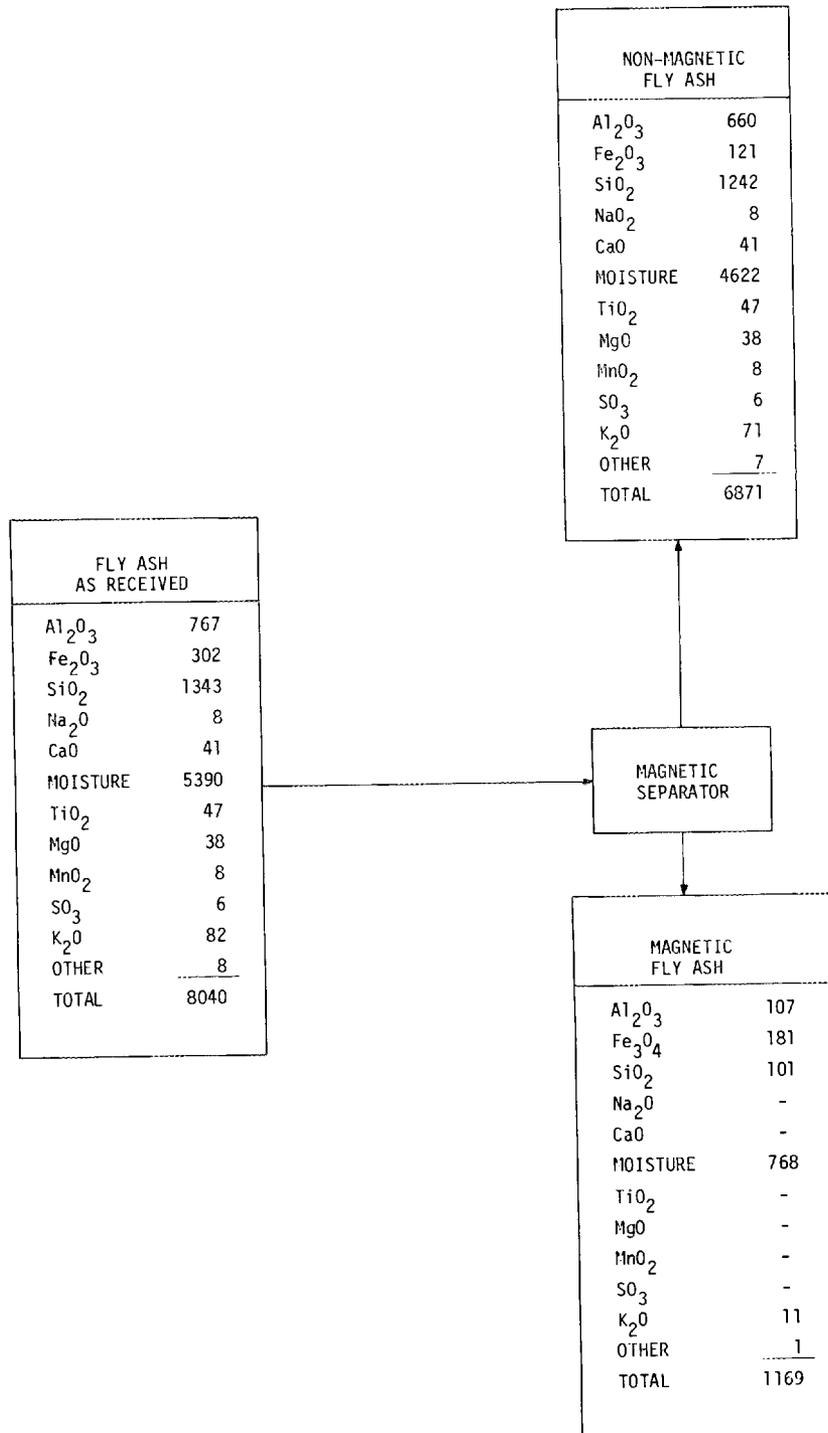


Fig. B-1. Material balance for magnetic separation section, salt-soda-sinter process (tons/day).

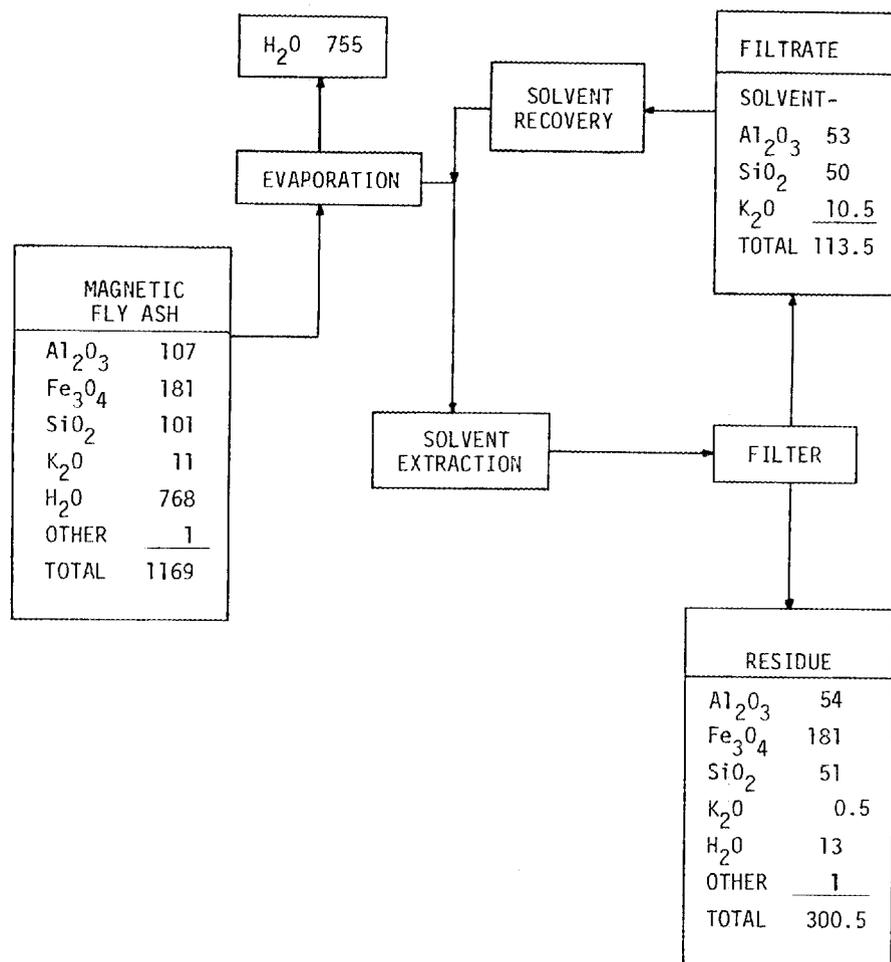


Fig. B-2. Material balance for magnetic iron purification section, salt-soda-sinter process (tons/day).

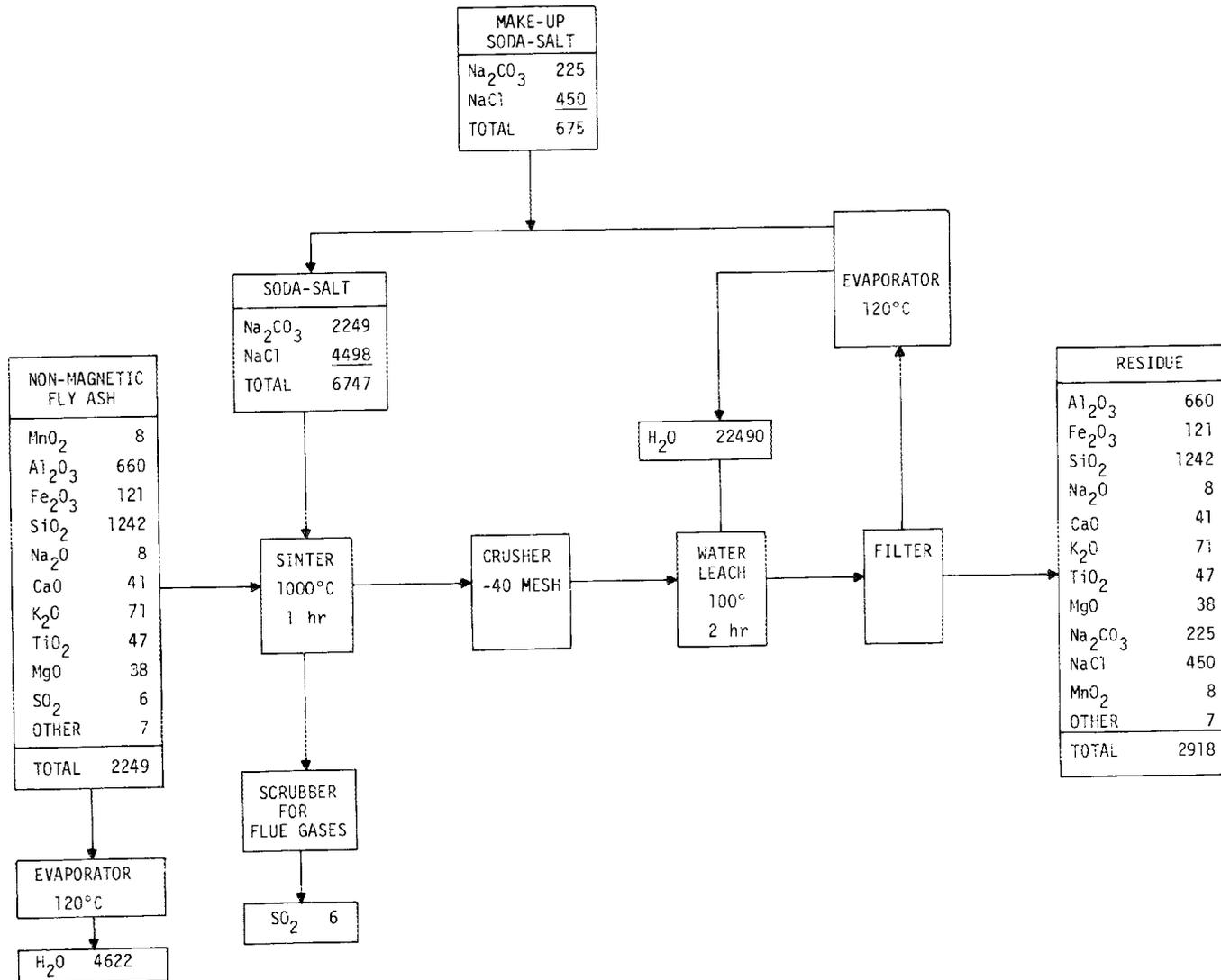


Fig. B-3. Material balance for sinter water leach section, salt-soda-sinter process (tons/day).

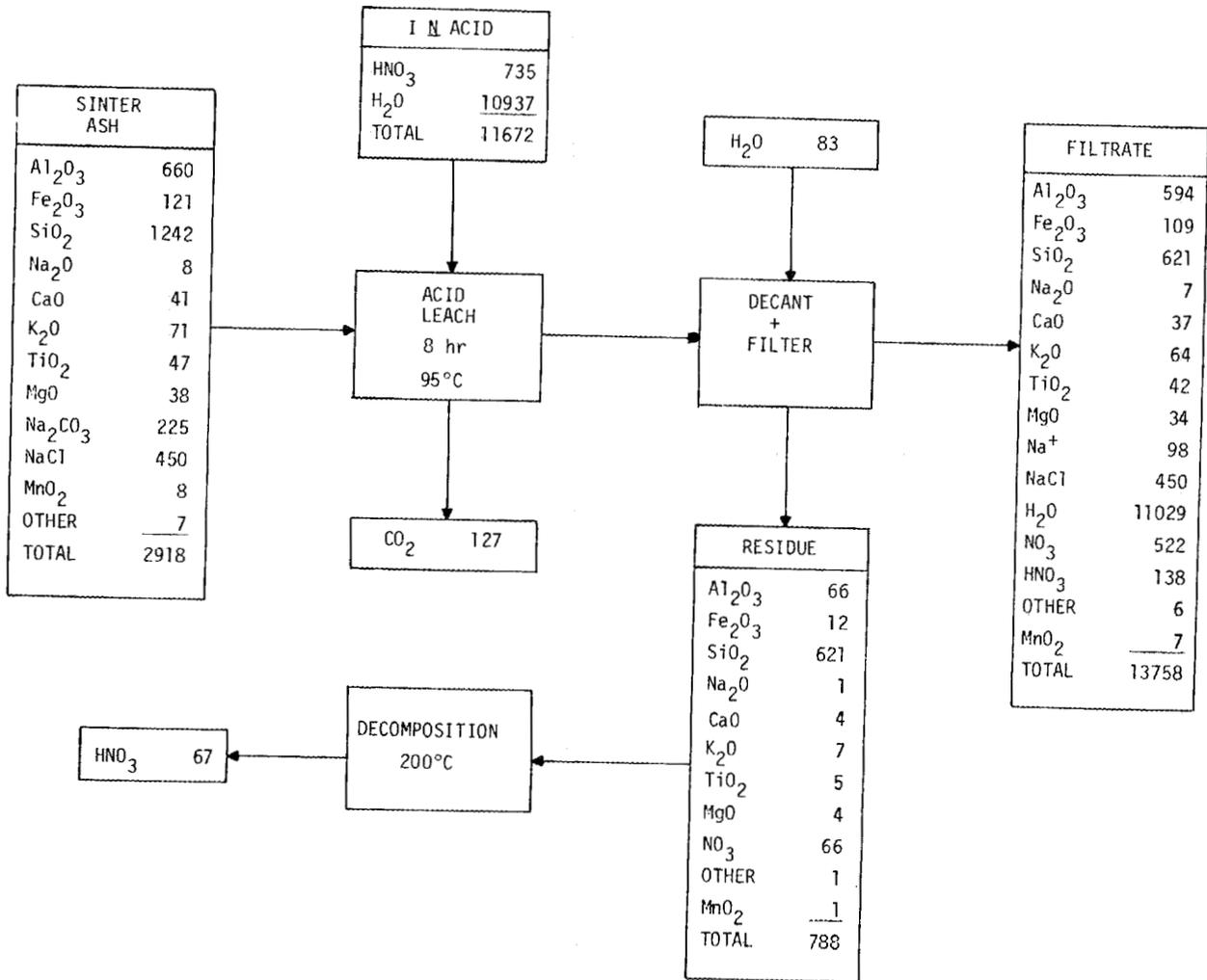


Fig. B-4. Material balance for the acid leach section, salt-soda-sinter process (tons/day).

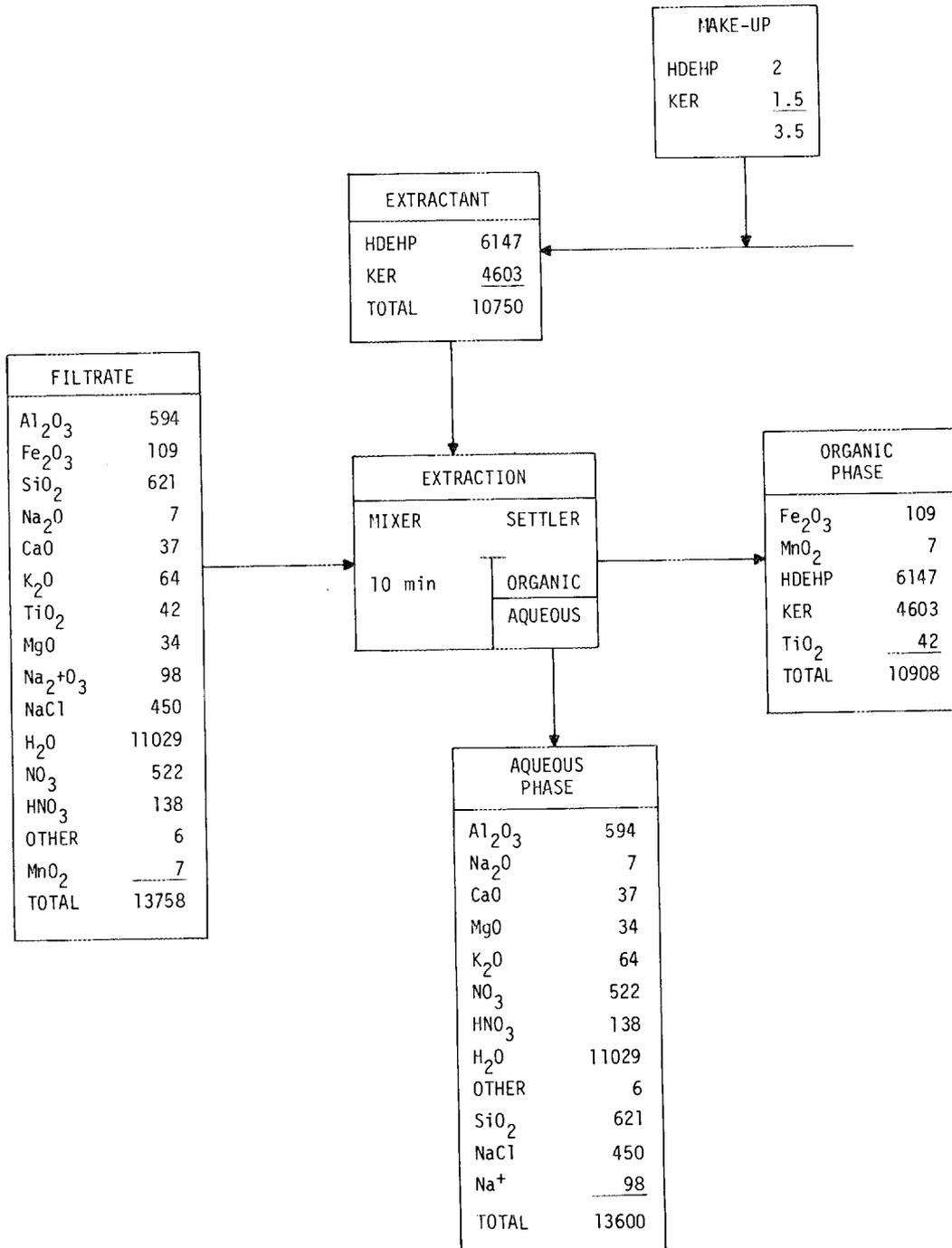


Fig. B-5. Material balance for the solvent extraction section, salt-soda-sinter process (tons/day).

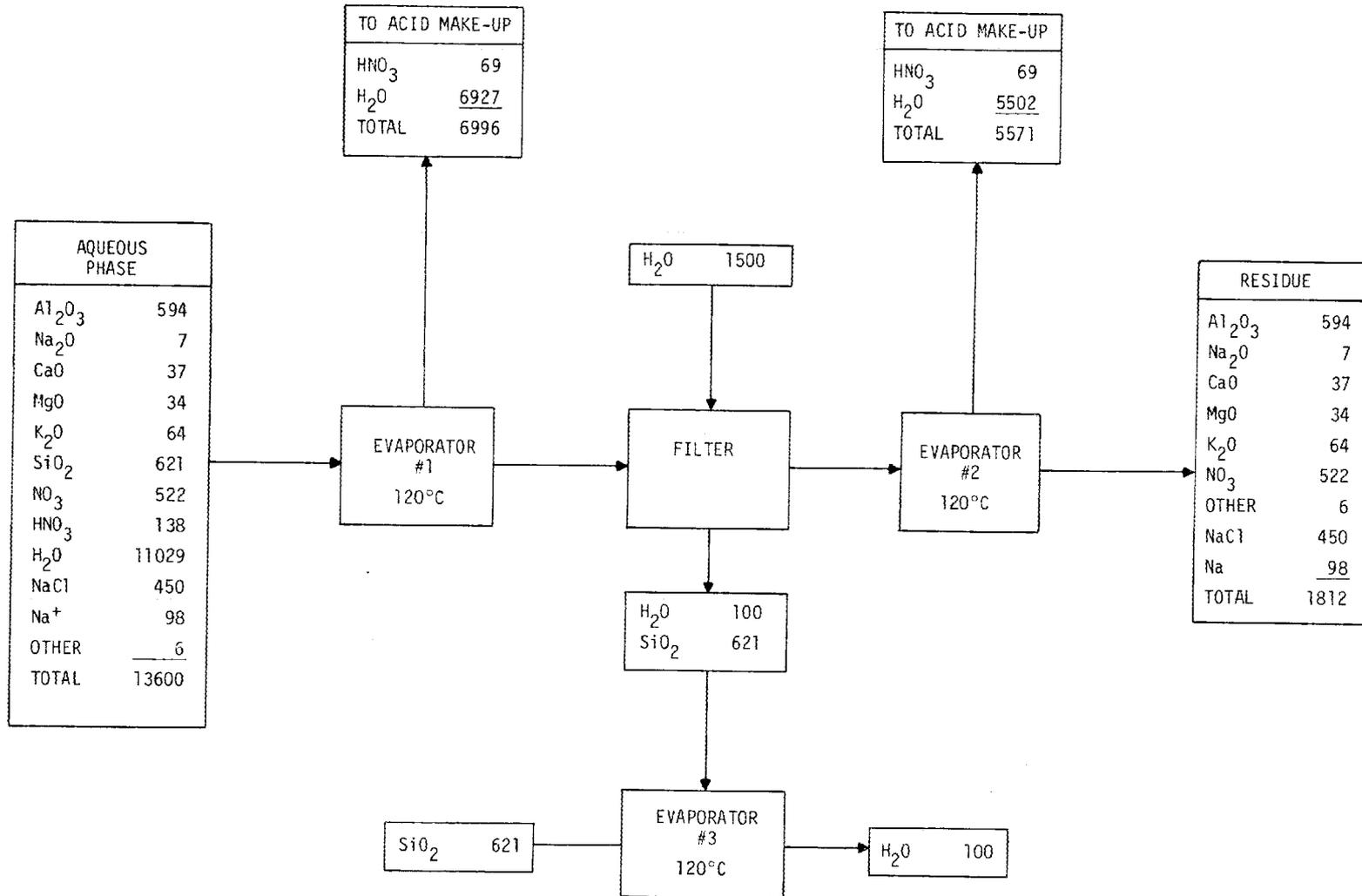


Fig. B-6. Material balance for the silica gel section, salt-soda sinter process (tons/day).

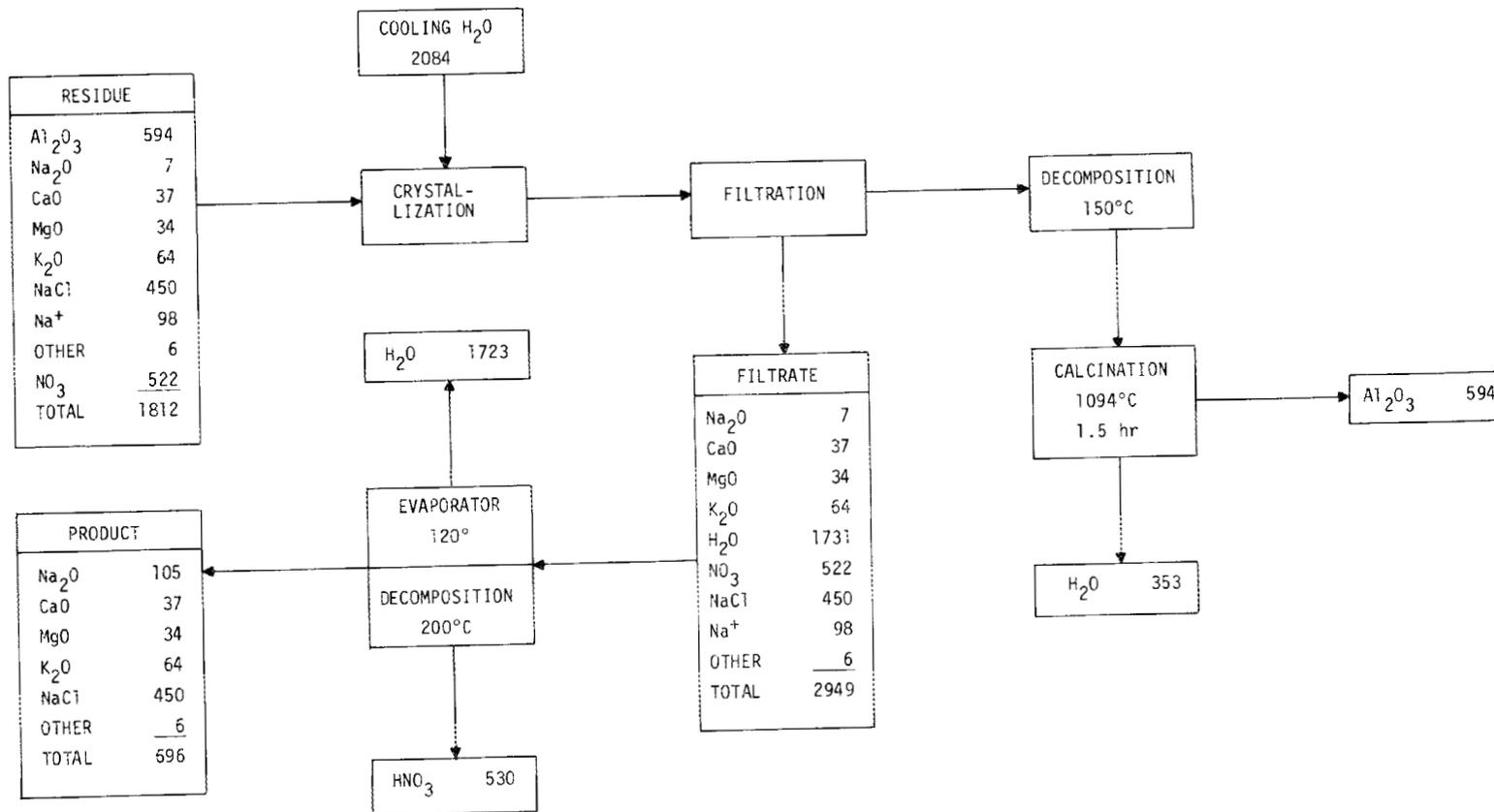


Fig. B-7. Material balance for the crystallization and calcination sections, salt-soda-sinter process (tons/day).

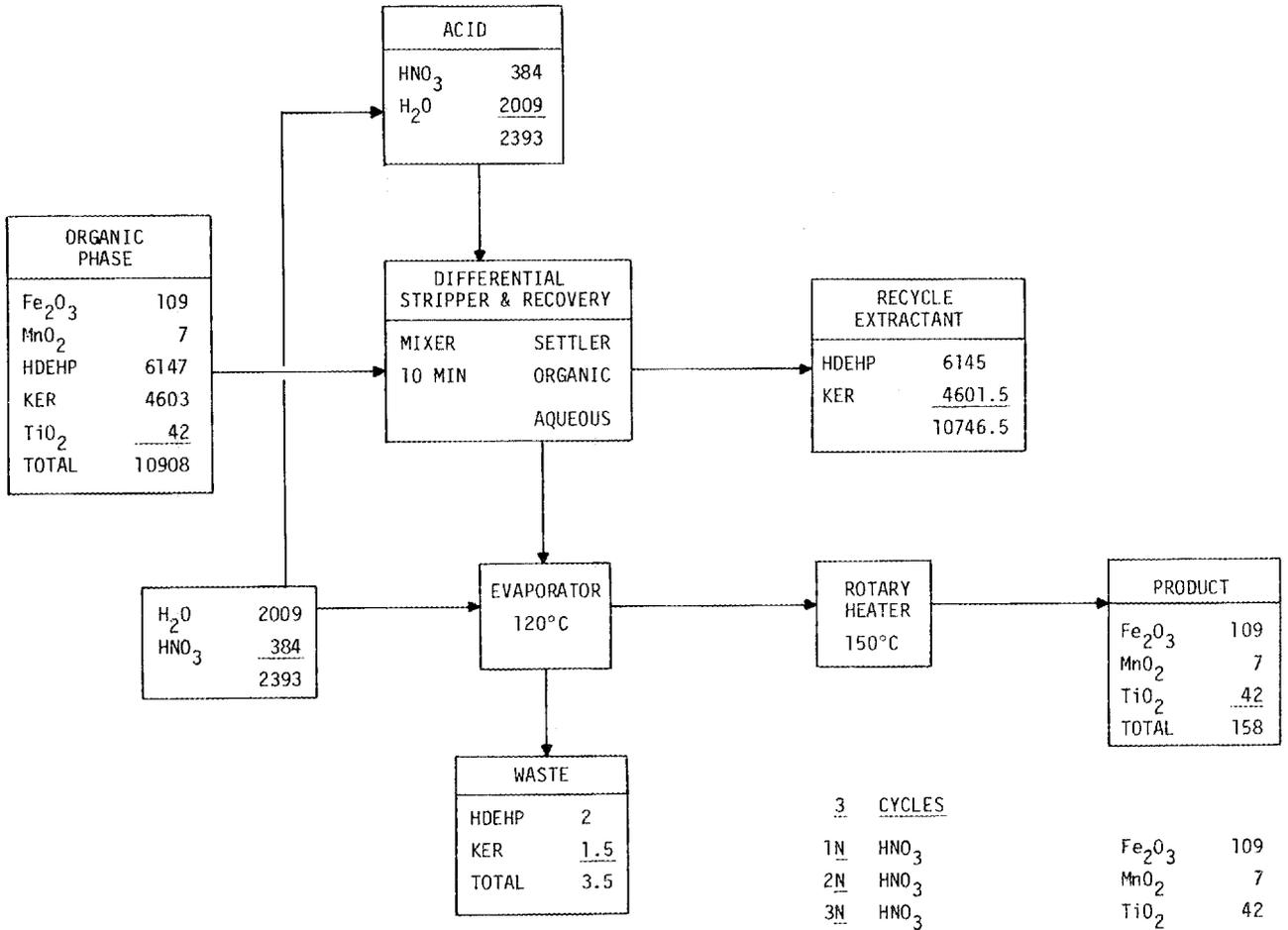


Fig. B-8. Material balance for the mineral stripping section, salt-soda-sinter process (tons/day).

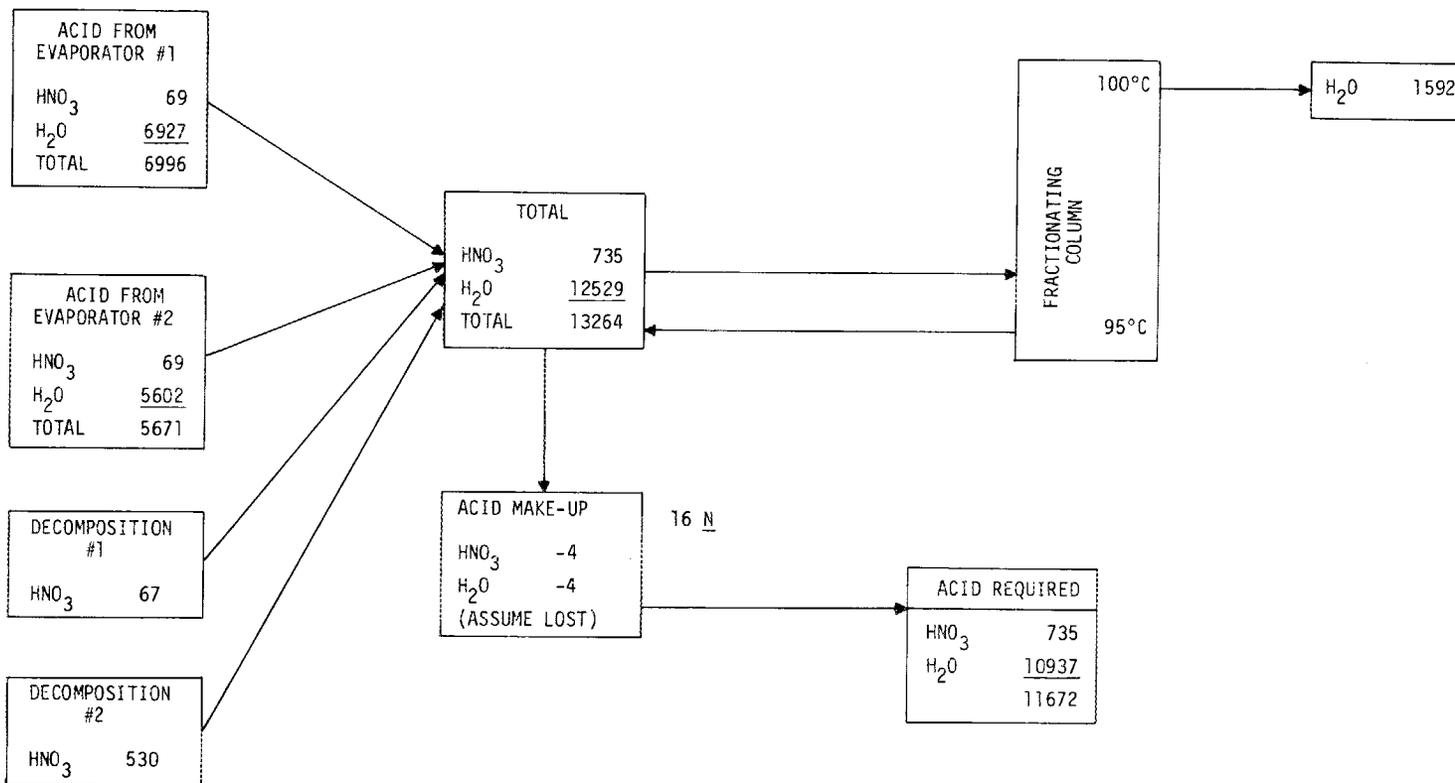


Fig. B-9. Material balance for the acid recovery section, salt-soda-sinter process (tons/day).

6.3 Appendix C: Cost Analysis and Material Balance for the Nitric Acid Leach Process

A cost estimate of a nitric acid leach process to produce iron oxide, alumina, titanium oxide, and manganese oxide from 1×10^6 tons of fly ash per year (dry basis) is summarized below. All costs are in 1977 dollars.

Total facility cost	\$58,006,000 ^a
Total operating costs	\$22,448,800
Income from sale of products	\$31,114,425

^aAdd 30% if land and utilities are required.

The various costs are detailed in Tables C-1 through C-4. Material balances are shown in Figs. C-1 through C-8.

Table C-1. Breakdown of facility cost

Magnetic Fly Ash Separation	
Construction	\$2,009,000
Engineering	502,000
Contingency	<u>1,256,000</u>
Total	\$3,767,000
Nitric Acid Leach Section	
Construction	\$28,927,000
Engineering	7,232,000
Contingency	<u>18,080,000</u>
Total	\$54,239,000

Table C-2. Operating costs of nitric acid leach process

Solvent extractant	55 tons/day x 365 days/year x \$188/ton	\$ 4,204,800
HDEHP	2 tons/day x 365 days/year x \$3,750/ton	2,737,500
Kerosene	1.5 tons/day x 365 days/year x \$100/ton	54,750
Nitric acid	12 tons/day x 365 days/year x \$375/ton	1,642,500
Electric power	(800 kW)(24 hr/day)(365 days/year) (\$0.015 kWhr)	1,051,200
Steam	(40,000 lb/hr)(24 hr/day)(365 days/ year)(\$0.002/lb)	700,800
Natural gas	(600,000 ft ³ /hr)(24 hr/day)(365 days/ year)(\$0.001/ft ³)	5,256,000
Operating labor	10 at \$25,000 x 4 shifts	1,000,000
Maintenance	10% initial cost	<u>5,800,600</u>
		\$22,448,150

Table C-3. Income from sale of products

Iron pellets	300 tons/day x 365 days/year x \$30/ton	\$ 3,285,000
TiO ₂	16 tons/day x 365 days/year x \$530/ton	3,095,200
Alumina	429 tons/day x 365 days/year x \$155/ton	24,270,675
Iron	79 tons/day x 365 days/year x \$5/ton	144,175
MnO ₂	5 tons/day x 365 days/year x \$175/ton	<u>319,375</u>
		Total \$31,114,425

Table C-4. Equipment cost summary

Item	Cost (\$)	
	Material	Labor
<u>Magnetic Separation System</u>		
Slurry pipe	180,000	14,400
Pumps	18,000	1,152
Magnetic separator, three-stage	180,000	4,860
Clarifier, thickeners	65,000	8,280
Dryer, steam heated	100,000	3,150
Solvent extractor contactor	180,000	8,100
Recycle pumps	15,600	1,296
Solvent storage tanks	255,000	a
Injector pumps, 0 to 60 gpm	10,500	432
Unloading pumps, 900 gpm	9,000	432
Screw feeder	3,900	324
Cone pelletizer	65,000	288
Binder injector, spray unit	5,000	216
Tunnel dryer	30,000	1,440
Pellet hopper	60,000	a
Structures and foundations	43,500	13,500
Electrical	8,000	8,100
Piping-steam-gas-process	15,000	9,000
Instrumentation	21,000	13,500
Miscellaneous	126,500	8,830
	LSPC direct.... \$1,391,000	\$97,300
	Overhead + administration.....\$ 520,700	
	LSPC total.....\$2,009,000	
<u>Nonmagnetic System</u>		
A. Nitric Acid Leach		
Acid storage tanks	38,000	10,800
Acid pumps	7,000	900
Acid makeup pumps	3,000	432
Mixers	27,000	1,620
Thickener	133,400	14,400
Slurry feeder	42,000	1,080
Acid leach tanks	1,680,000	383,994
Reflux condenser	1,200,000	180,000
SO ₂ scrubbers	140,000	43,209
Leach pumps	112,000	2,880
Leach tanks	600,000	288,000

^aFabricated in place.

Table C-4. (continued)

Item	Cost (\$)	
	Material	Labor
Residue dryers	720,000	21,600
Condenser	112,000	5,760
Recycle acid pumps	43,200	2,880
Residue conveyors and loader	600,000	a
Filtrate pumps	64,000	4,320
Evaporators	72,000	216,000
Condensers	204,000	4,050
Acid return pumps	36,000	2,160
Acid storage tanks	376,000	a
Sludge tanks	450,000	21,600
Residue conveyor	450,000	a
Filtrate pumps	84,000	2,160
Organic storage tank	36,000	5,400
Organic unloading pumps	9,000	720
Organic metering pumps	13,500	1,080
Kerosene storage tanks	13,500	3,240
Unloading pumps	4,600	288
Kerosene metering pumps	3,000	144
Residue tanks	48,000	a
Separator tanks	44,000	115,200
Water transfer pumps	25,600	1,440
Organic transfer pumps	18,920	1,440
Evaporators	96,000	288,000
Condensers	176,800	216,000
Acid return pumps	36,000	1,440
Settling tank	48,000	288,000
Drum flaker dryer	200,000	9,000
Weighing and bagging station	48,000	1,080
Filters	16,200	432
Evaporator	48,000	21,600
Decomposition evaporator	7,000	2,232
Condensers	52,000	2,700
Acid recycle pumps	6,800	720
Evaporators	136,000	10,800
Condenser	116,000	10,800
Acid recycle pumps	21,600	1,440
Rotary calciner	260,000	1,500
Conveyor and coolers	26,000	1,800
Weigh hopper and loaders	48,000	4,320
Stripper tank	54,000	172,800
Recycle pumps	34,800	1,440
Water feed pumps	23,200	972

^aFabricated in place.

Table C-4. (continued)

Item	Cost (\$)	
	Material	Labor
Evaporator	76,000	10,800
Condenser	60,000	3,600
Recycle acid pump	21,600	1,440
Rotary heater	19,600	2,880
Conveyor cooler	12,000	2,880
Weigh hopper and loader	24,000	4,140
Structures and foundations	494,000	198,000
Electrical power	742,000	297,000
Piping-steam-gas	1,731,000	630,000
Instrumentation	1,483,000	49,000
Building	500,000	83,000
Miscellaneous	<u>1,453,679</u>	<u>494,226</u>
	LSPC direct....	\$15,990,300
	Overhead + administration.....	\$ 7,499,800
	LSPC total.....	\$28,927,000

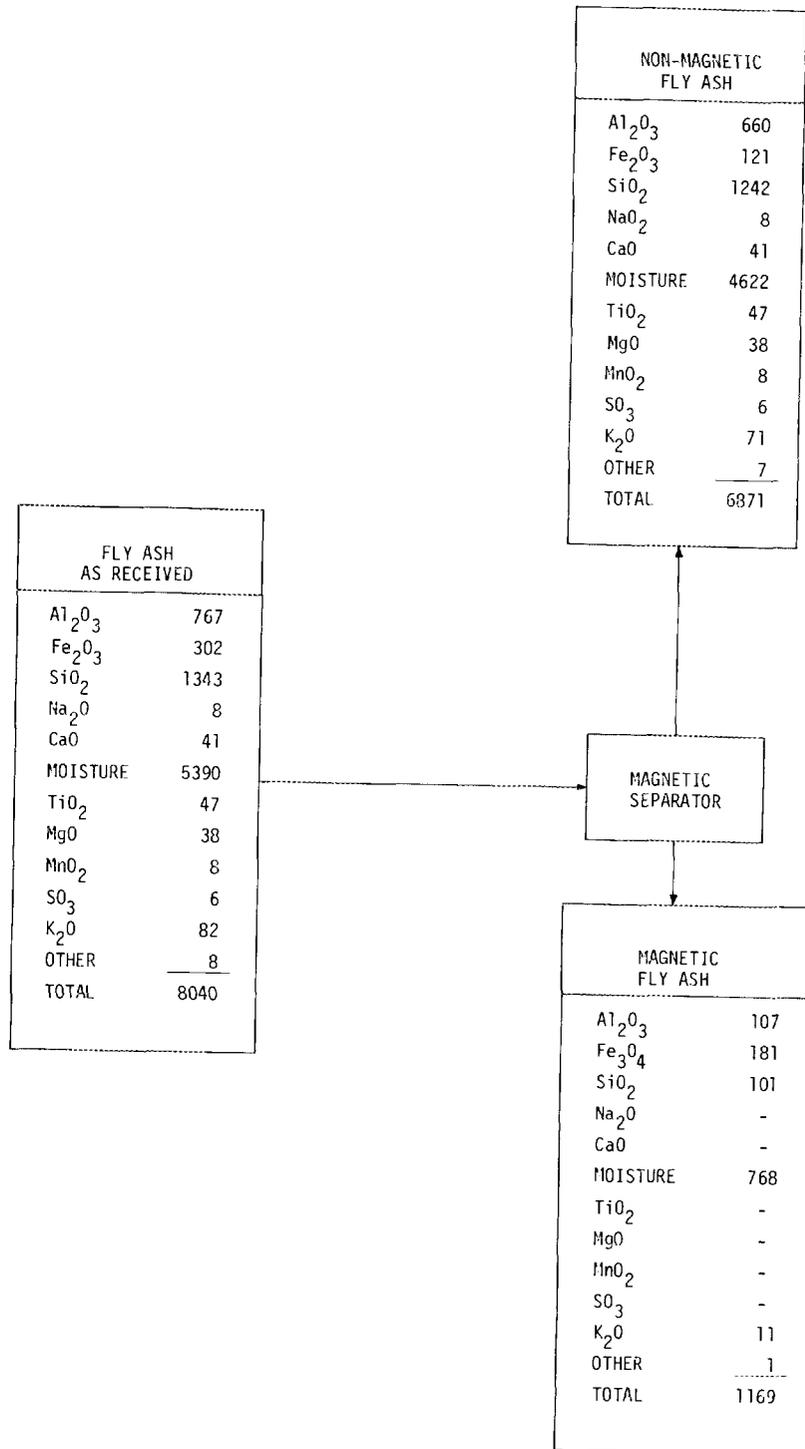


Fig. C-1. Material balance for the magnetic separation section, nitric acid leach process (tons/day).

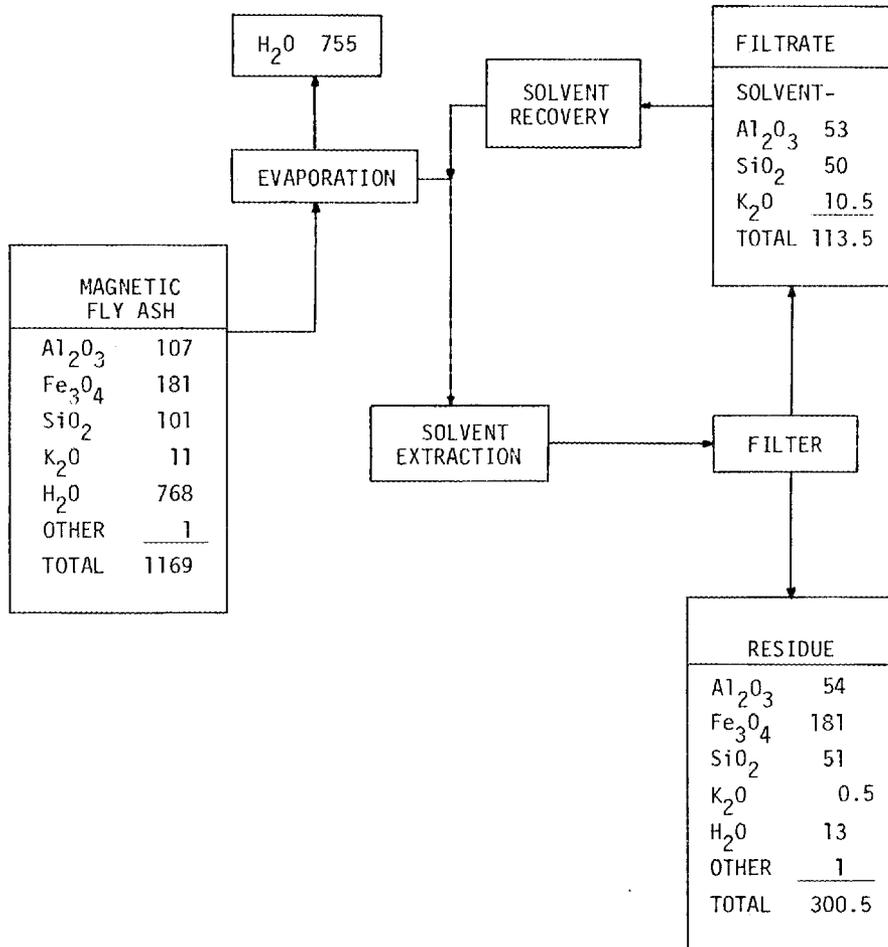


Fig. C-2. Material balance for the magnetic iron purification section, nitric acid leach process (tons/day).

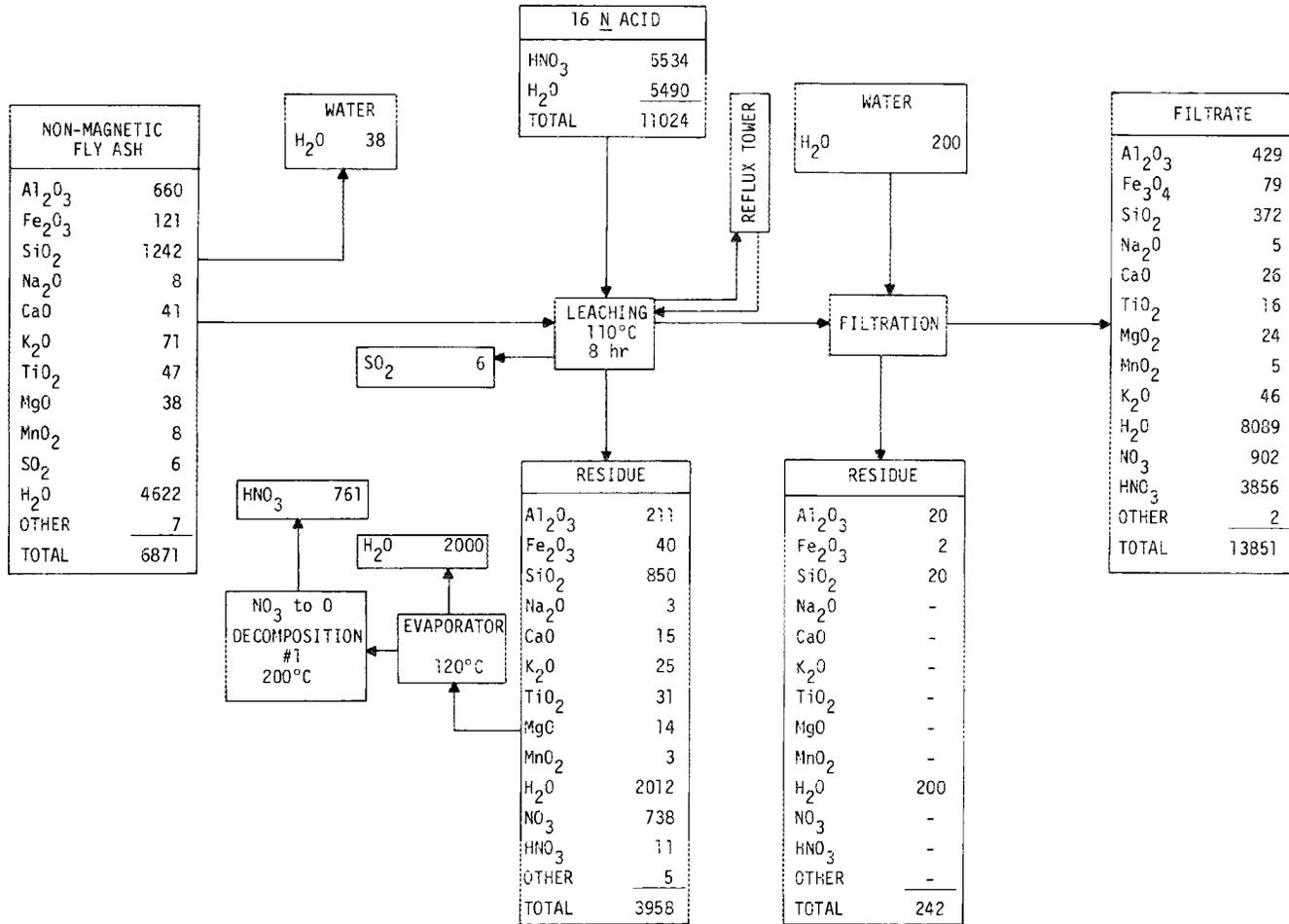


Fig. C-3. Material balance for the acid leach section, nitric acid leach process (tons/day).

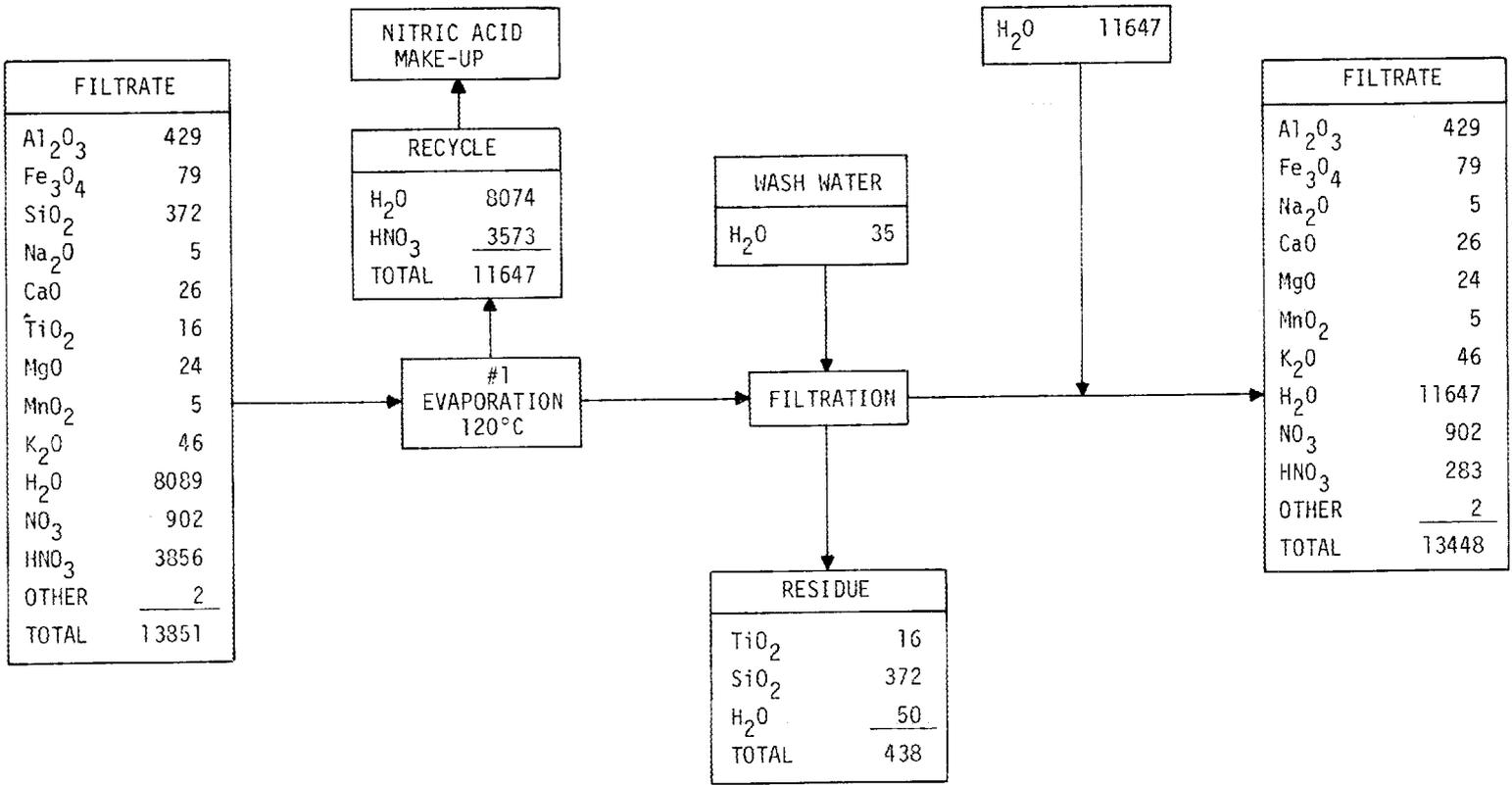


Fig. C-4. Material balance for the evaporation and filtration sections, nitric acid leach process (tons/day).

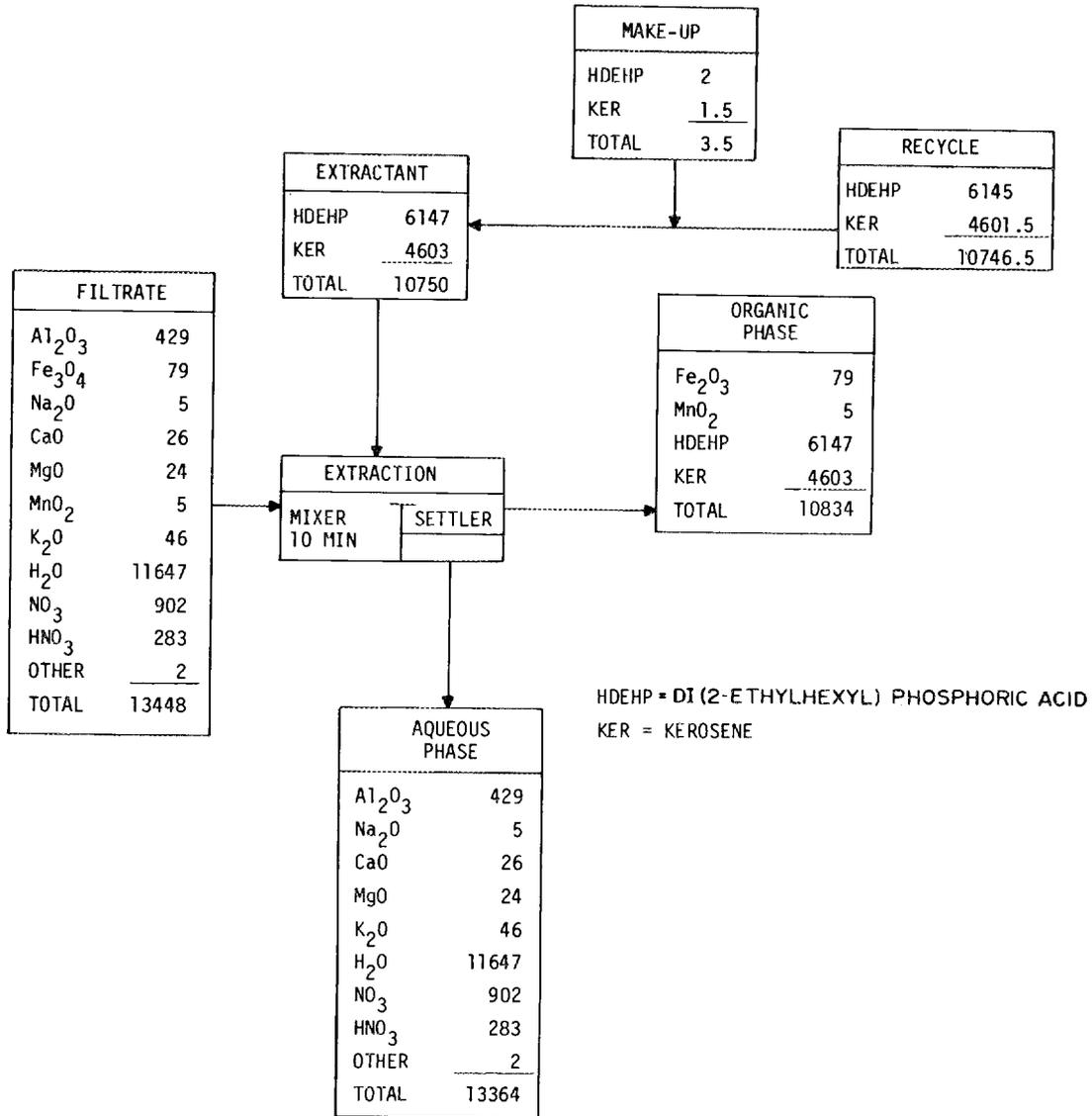


Fig. C-5. Material balance for the solvent extraction section, nitric acid leach process (tons/day).

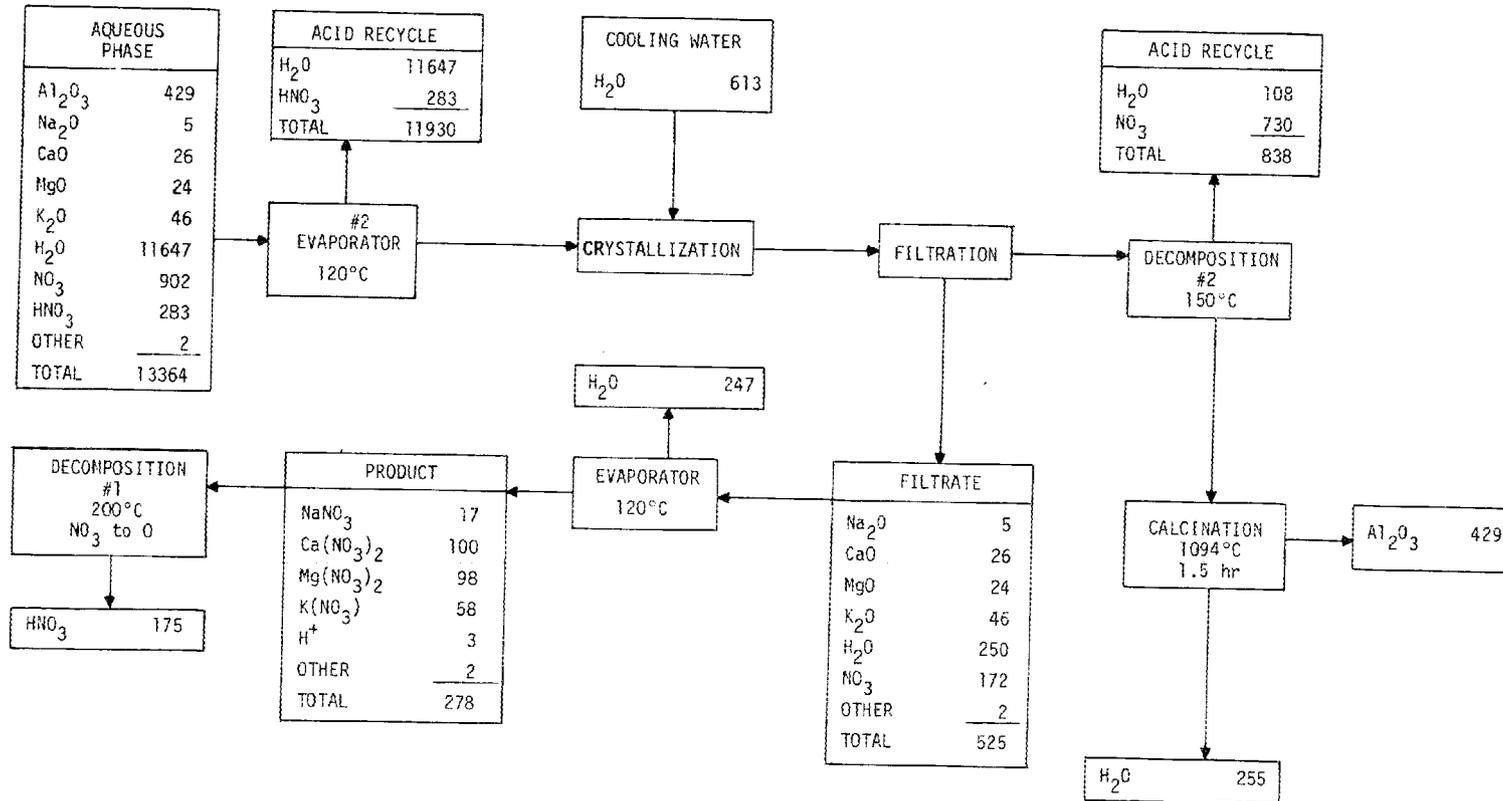


Fig. C-6. Material balance for the crystallization and calcination sections, nitric acid leach process (tons/day).

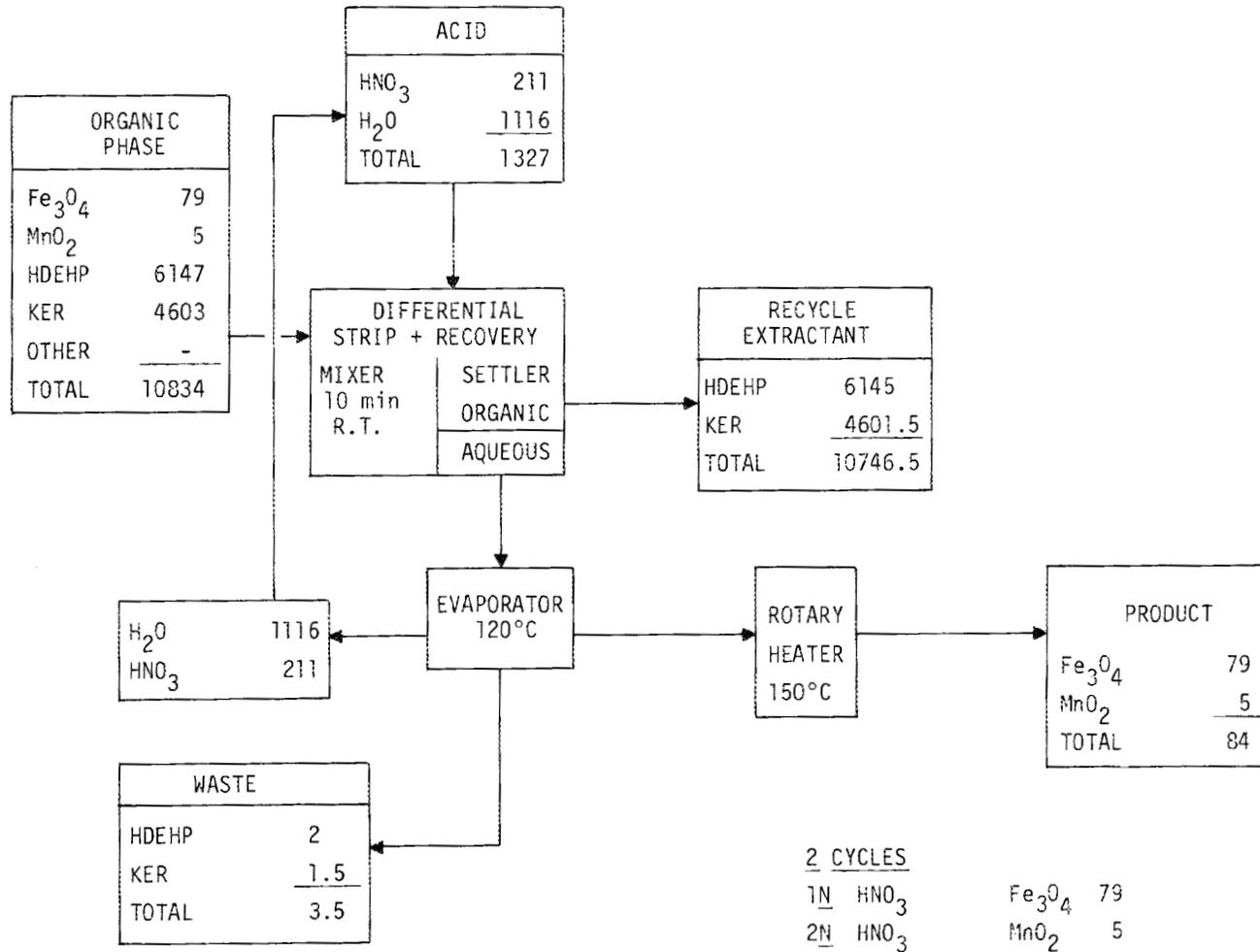


Fig. C-7. Material balance for mineral stripping section, nitric acid leach process (tons/day).

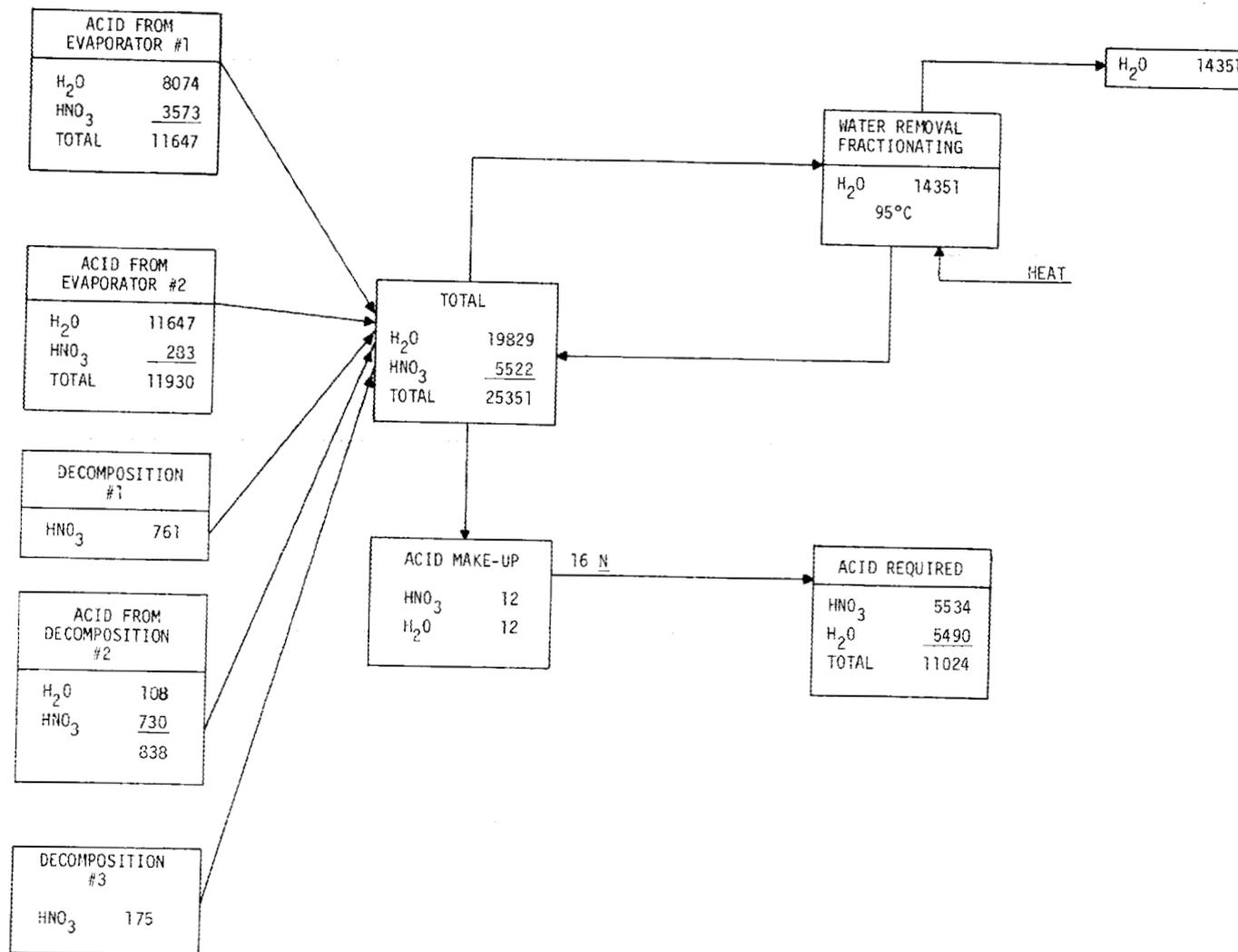


Fig. C-8. Material balance for the acid recovery section, nitric acid leach process (tons/day).

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