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ALUMINA FROM CLAY - A NITRIC ACID PROCESS

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An overview of the operational sequencing and technical background of Reynolds Metals Company's patented process for the recovery of metallurgical grade alumina from kaolin clay is presented.

The process can use high iron kaolin clays of no present economic value, is insensitive to varying potash content, and minimizes hazardous waste discharges to the environment. It requires about 17 mm BTU/ton alumina (19.8 GJ/tne) net heat input to process streams, of which only about 0.5 mm BTU (0.6 GJ) need be supplied by oil or natural gas.

Each of the major operations that are combined to form the process uses well-known equipment and commercially available construction materials and is supported by substantial amounts of pilot scale and/or laboratory data developed by a team of chemists and engineers.

Introduction

This paper presents an overview of the Reynolds Metals Company process for the extraction of alumina from kaolin clay with nitric acid. The process is disclosed in detail in various issued and pending U.S. patents (2) Alumina Production by Nitric Acid Extraction of Clay; (3) Basic Aluminum Nitrate Crystallization; (4) Decomposition of Aluminum Nitrate; (5) Nitric Acid Reconstitution; (6) Clay Preparation; (7) Process for the Crystallization of Aluminum Nitrate Nonahydrate; and (8) Removal of Chromium from Aluminum Nitrate.

Since about 1968 in the laboratory, and frequently in the pilot plant, Reynolds chemists and engineers cooperatively have studied the physical and chemical operations required throughout the fully-integrated process. The data obtained during the investigation are thought to provide an adequate base for the design and operation of a large scale pilot or semi-commercial plant.

Process Summary

Important processing operations of the Reynolds Nitric Acid Process are shown in block diagram form on Figure 1, along with selected stream quantities from a mass balance flow sheet, net-heat-to-process values from an energy balance, and interfaces with the environment for one unit of Al_2O_3 product. Mass quantities can be read as tons or tonnes, heat values in mm BTU/ton and GJ/tonne and volumes in ft^3/ton and m^3/tonne Al_2O_3 product. Net-heat-to-process values are given to avoid confusion in methods of heat recovery, temperature of stack gases, etc.

Particular distinguishing features of the Reynolds Process include (1) production of rounded, sized kaolin pellets which can be calcined in fluid beds using inbed combustion of coal with minimum attrition; (2) countercurrent leaching and washing in fixed-bed extractors with attendant high efficiency and minimum sludge formation, which particularly permits washing the spent, undegraded pellets to any desired residual level of HNO_3 without need to evaporate the wash liquor; (3) precipitation as hematite of just enough iron to permit specification iron values to be obtained by fractional crystallization; (4) crystallization of aluminum nitrate nonahydrate (ANN) from acid-deficient media, and washing the crystals with water instead of concentrated HNO_3; (5) partial decomposition in a 2-stage low temperature process producing undecomposed vapors that can be condensed directly to nitric acid liquors with recovery of the heat of condensation at temperatures high enough for reuse; and (6) reconstitution of NO_x values in a new process which minimizes compressor loads and permits input of makeup NO_x from oxidation of ammonia at atmospheric pressure.

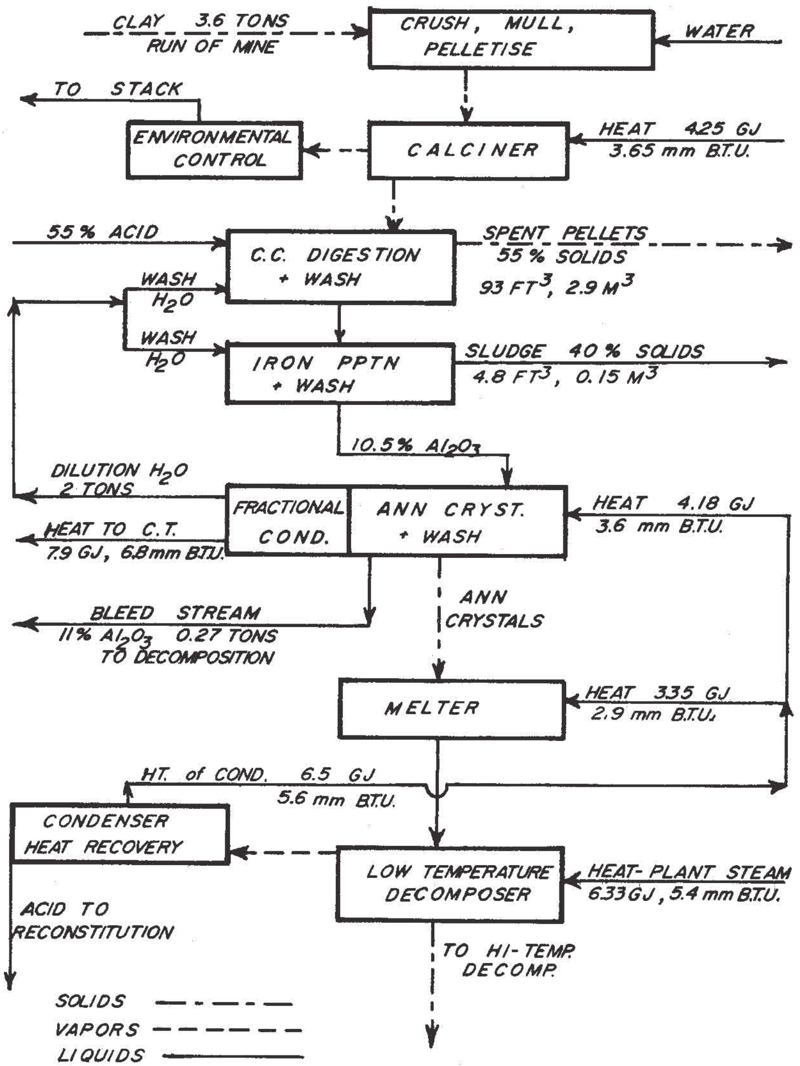
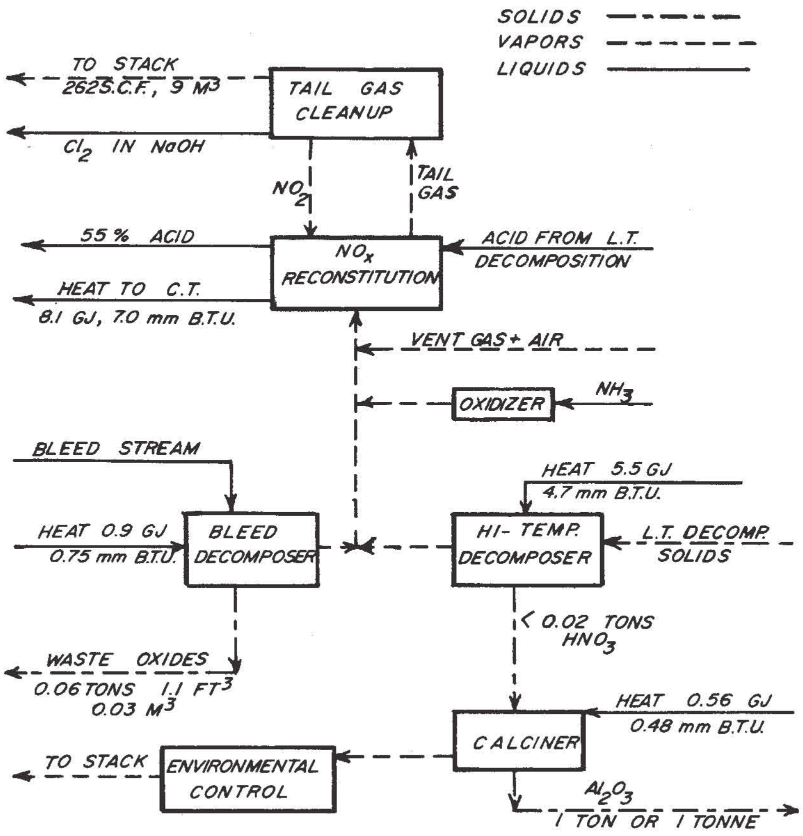


FIG. 1
NITRIC ACID PROCESS
BASIS: 1 TON or 1 TONNE Al_2O_3



NET HEAT TO PROCESS SUMMARY

	GJ/TNE.	mm B.T.U./TON
TOTAL INPUT	26.3	22.6
RECOVERED	6.5	5.6
NET REQUIRED	19.8	17.0
HEAT TO C.T.	16.2	13.9

VOLUMES - M^3/TONNE, FT^3/TON

FIG. 1 (Cont.)
NITRIC ACID PROCESS
BASIS: 1 TON or 1 TONNE Al_2O_3

Description of Process Components

Preparation of Pellets

Run of mine kaolin ore comprising about 15% to 20% moisture, about 0.5% to 5% Fe_2O_3, and K_2O, P_2O_5, and other trace element values is crushed to nominal size, fed directly to a muller, and blended with recovered calcined clay dust and water to a moisture content of about 20%. Little or no need for partial drying of the ore is expected.

The mulled mixture is converted to sized pellets by passing through hammermills equipped with 360° screens of selected apperture. We have produced many hundreds of pounds of such pellets with a Stokes laboratory tornado mill and have observed only nominal wear on the knives and the screens. The resulting pellets are rolled in a rolling drum, in the presence of small amounts of warm air to prevent agglomeration, to form substantially round pellets with hardened surfaces. Proper control of moisture in the mulled clay and elimination of agglomeration in the rolling drum permits production of product balls that do not require scalping of either oversize or undersize. The rounded, surface hardened pellets are dried, and fired in fluid beds heated by the inbed combustion of powdered coal at temperatures up to about 1500°F (815°C).

The calciner off-gases are scalped of coarse particulate matter and scrubbed to remove SO_x and fine fly ash before discharging to the atmosphere. The recovered particulate matter is recycled to the pelletizing operation.

Extraction

The calcined pellets are leached and washed in a series of stationary-bed extractors inter-connected for counter current flow with heated 55% to 57% nitric acid from the acid recovery plant and with sufficient dilution water to provide extract liquor averaging 10% to 11% alumina and less than 6 to 1 mol ratio of NO_3 to Al_2O_3. Solids hold up time is about 2 hours in digestion and 2 to 3 hours in the washing portion of the extractors. Alumina extractions greater than 95% have been obtained in laboratory and pilot-scale batch-counter-current extractions and a shrinking-core kinetic model has been fitted to the extraction data. The degree of washing achieved, i.e., the concentration of HNO_3 in the washed-pellet liquor, can be determined by the number of washing stages provided. Laboratory data show concentration equilibration between pellets and quiescent liquor in only 15 minutes and that no insoluble nitrates are formed. The operation is expected to be self-supported thermally by heat of condensation recovered from the approximately 1 ton of vapor produced per ton of alumina digested.

Nitrates are not bound to the solids and residual nitrates in the void volume water are essentially all HNO_3. The pellets, which are not disrupted or mechanically abused in the beds, maintain their original bulk volume and drain easily and quickly to about 55% solids. The pellets are expected to be satisfactory for backfill in spent clay mines. If desired, they may be crushed relatively easily to reduce the bulk volume. Acid vapors produced during the leaching operation are collected and recycled to the leach acid.

Iron Removal

During most of the digestion cycle some of the rich-liquor digestion stages are deficient in acid. Some of the iron dissolved in the lean stages precipitates as acid-insoluble hematite that passes out with the spent silica solids, leaving an extract liquor containing up to about 1/2% dissolved Fe_2O_3. The liquor is collected unfiltered and uncooled in the first tank of the iron removal system and blended with hematite-coated silica solids, recovered from the down-stream thickener, to enhance the rate of iron precipitation. Since laboratory data show the iron removal system requires an effective liquor hold-up time in contact with seed of at least four hours, and that additional time is not detrimental, the system can be made large enough to provide surge and blending capacity to smooth cyclic fluctuations in the concentration of acid in the digest liquor. The system also is insensitive to the input loading of dissolved iron. Thus it does not impose control problems in digestion or mining. The process can use without penalty high-iron clays that have no other value, and selective mining and/or ore blending to maintain a constant iron level in the feed should not be needed.

Final dissolved iron levels in the liquor are about 0.025%, sufficiently low to achieve specification in fractional crystallization. After treatment is completed the suspended solids content is thickened and recycled to the fresh extract receiver and the overflow is filtered to remove small amounts of carry-over solids and colloidal silica and forwarded to fractional crystallization.

A portion of the settled solids, which have been found to contain about 2500 ppm chemically-bound nitrate, equivalent to the system input are washed with a portion of the available dilution water, centrifuged to about 40% solids, and disposed of with the spent clay pellets.

Fractional Crystallization

A fractional crystallization arrangement for producing alumina with less than 0.005% P_2O_5 is shown in Figure 2. Re-dissolving and recrystallizing the product can reduce the P_2O_5 to <0.001%. Feed liquor enters the system at Unit 1 and mother liquor is purged from Unit 1 to Unit 2 to Unit 3 to the impurity bleed stream. Crystals formed in each unit are

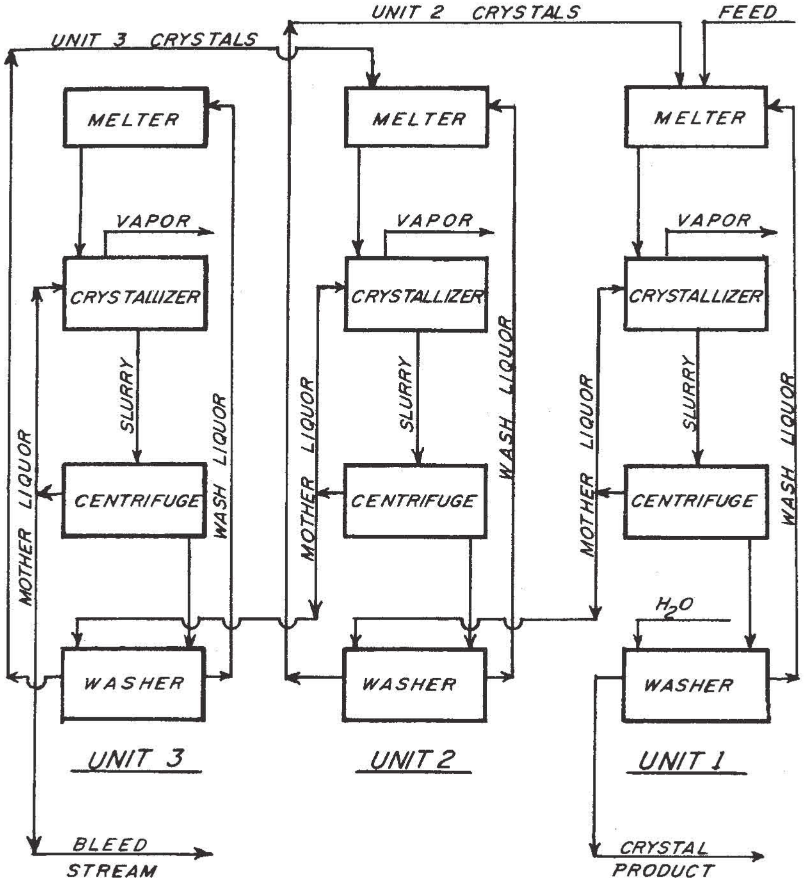


FIG. 2

ANN CRYSTALLIZATION

washed and move forward from Unit 3 to Unit 2 to Unit 1. Unit 1 product is washed with water and forwarded to melting and decomposition. Vapors from the vacuum evaporative crystallizers are condensed in fractional condensers.

Product purity, pre-evaporation requirements and the system energy requirements are affected strongly by the purge rate from Unit 1, moderately by the purge rate from Unit 2, and scarcely at all by the bleed stream rate within the range of about 1% to 5% or so of the feed alumina. Overall plant energy efficiency favors a minimum bleed stream. Data shown on Figure 1 have been calculated for a bleed of 0.03 tons Al_2O_3 per ton Al_2O_3 product and Unit 1 and 2 purge rates that require no pre-evaporation. Mother liquor in the crystallizer is controlled on the acid-deficient side of neutral by adding nitric acid to each dissolver as needed. Improper purge rate settings also can force addition of water to these dissolvers. A computer algorithm of the mass, energy and impurity balances is useful for operation as well as design.

The crystallizers operate within the range of about 30 to 60°C and may be allowed to float within this range as the temperature of the cooling water used in the fractional condensers varies. Heat for water evaporation is supplied in part by the heat of crystallization of the aluminum nitrate nonahydrate and in part by heat supplied to the dissolvers.

Separation factors SF, defined as the ratio of the impurity concentration in a 100% washed crystal to concentration in the crystal mother liquor, have been determined in laboratory experiments over the range of mother liquor concentrations from those in a bleed stream purging about 1% of the alumina to those providing specification alumina purity. ANN crystallization rates as high as 29 pounds per hour per cubic foot of slurry (470 kg/m^3/hr) were used. The observed SF values were sufficiently low to permit achieving required product purity.

Excellent washing in each stage is required. The relation $A=P\ (SF+(1-E)\ L/S)$, in which

A = impurity concentration in the washed cake;
P = impurity concentration in the mother liquor;
E = fraction of mother liquor displaced by wash;
L/S = liquid to solids weight ratio in the cake;

defines the balance over the liquid and solid phases for a crystallization and washing stage. The term (1-E) L/S must be kept small, by choice of equipment and methods, to achieve the required purification in a reasonable number of stages. Also, the L/S of the product crystals determines the concentration of the recovered leach acid. Multiple-stage washing centrifuges are desirable.

Crystallizer vapors containing up to about 1/2% nitric acid are condensed in fractional condensers to obtain a low-acid-content water stream for reuse as dilution water and washing the nonahydrate crystals and an acidic condensate which is used for supplying makeup water in acid recovery.

Low Temperature Decomposition

Washed aluminum nitrate nonahydrate crystals are melted, and then decomposed to a solid, infusible basic aluminum nitrate hydrate in a 2-stage process which can be operated with plant steam. The 50% to 55% nitric acid vapors obtained are condensed at their boiling points in heat recovery means and the heat of condensation is available to use in crystal melting and crystallization.

In the first stage the liquor is evaporated in a single-pass, evaporation-in-the-tube long-tube-vertical evaporator to 20-22% alumina. Overall heat transfer coefficients in excess of 100 BTU/ft^2/hr°F (570 W/m^2 °C) have been obtained. Vapors of 50% to 52% nitric acid were obtained at around 300°F (150°C), and 10 to 20 psig (1.7 to 2.4 bar) while feeding about 20 lbs/hr of molten ANN through a 0.25 inch o.d. x 30 ft. long Ti tube evaporator.

The hot liquor then is sprayed into a bed of partially decomposed pellets fluidized by recycling a portion of the nitric acid off-gases. The pellets grow by accretion of the liquid spray and are decomposed by heat supplied from condensing steam to an infusible basic aluminum nitrate hydrate pellet of controlled size, and vapors comprising around 55% HNO_3. The bed temperature is controlled to below about 400°F (200°C) to limit the degree of decomposition and avoid production of non-condensable NO_2 and O_2 and the vapors are condensed in heat recovery means.

High Temperature Decomposition

The pellets of basic aluminum nitrate hydrate are decomposed to alumina and NO_x, O_2, and water vapor in successive fluid beds operating respectively at about 750°F (400°C) and 1300 to 1400°F (700 to 760°C) fluidized by off-gases recycled from the 750°F decomposer. The gases, containing about 1/3 of the HNO_3 values present in the original ANN crystals, are sent to reconstitution and the decomposed alumina is calcined in a direct-fired fluid bed calciner. Fast-heat-up laboratory data simulating a fluid bed indicate that the concentration of residual nitrate in the product to calcination will be less than about 1% for a 1300°F decomposition, less than about 0.1% for a 1400°F decomposition, and essentially zero for a 1500°F (815°C) decomposition.

Laboratory studies of the decomposition of nitrates show that the conversion of NO_x to N_2 is negligible below about 800°F (427°C). At 1500°F (815°C) on 18-8 S.S., rates around 3 pounds of equivalent HNO_3 per day per 1000 ft^2 surface (1.5 kg HNO_3/day/100 m^2) were found. Decomposition tests on S.S. 316 have shown that a protective magnetite coating forms rapidly on the surface and adheres strongly until spalled off by cooling the surface to substantially lower temperatures. Nitrous oxide was not found in gases from decomposition on alumina, quartz or stainless steel, but was produced in large quantities during decomposition on zirconia.

Supplying indirect heat to these decomposers may be the most difficult and controversial operation required in the process. We presently favor use of recirculating sodium-potassium alloy (NaK) in view of its successful use in the waste calcining facility at the Idaho nuclear complex. However, no NaK system approaching the size needed for an alumina plant has ever been built.

Calcination

The decomposed alumina is calcined to a specified α-Al_2O_3 content (and corresponding H_2O content) in a fluid bed fluidized with about the stoichiometric amount of air, with heat supplied by in-bed combustion of fuel oil. The calcined product contains no nitrate.

It is well known that the oxygen combined in NO_x, at the high temperatures of calciner operation and even as low as 1200°F (650°C), is more reactive with fuels than is the oxygen of the air. Thus residual nitrate in the calciner feed will be reduced to N_2 by the fuel and NO_x concentrations in the calciner off-gases will not exceed the acceptably-low values obtained when firing stationary furnaces with near stoichiometric air. Therefore the calciner off-gases should not require additional NO_x control treatment to protect the environment or to meet legal requirements.

Purge Decomposition

The bleed stream from crystallization, comprising 0.01 to 0.03 tons alumina and about 0.03 tons impurity oxides per ton of alumina product and chloride and sulphate values entering the process, is thermally decomposed in steps similar to those for aluminum nitrate. Potash, phosphate, and other elements such as magnesium, copper, zinc, manganese, and iron have value in agriculture. If partially decomposed at about 750°F (400°C) it may be marketable as an approximately 5-5-10 fertilizer containing essential mineral elements. If found to be unmarketable, it would be calcined to remove all nitrate before disposal.

Reconstitution

The NO_x gases, and make up NO_x from atmospheric-pressure ammonia oxidation, are converted to nitric acid by absorption in recirculating 55% to 60% nitric acid solution as shown schematically in Figure 3. Calculations with a computerized NO_x absorption model indicate that, because of the high reactant concentrations in these gases, over 90% of the NO_x values can be converted rapidly to nitric acid at atmospheric pressure in relatively small, packed absorption columns operating with the large liquid-to-gas ratios required to remove the heat of reaction.

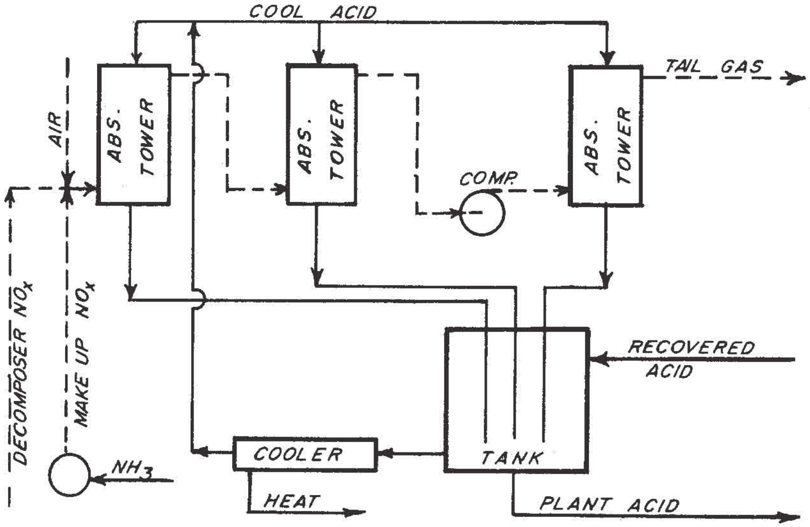


FIG. 3

NO_x RECONSTITUTION

The residual NO_x gas from atmospheric absorption is compressed to 3 to 6 atmospheres and reconstituted to nitric acid in a high pressure packed tower also operating with a large liquid to gas ratio. Off-gases from this tower are washed with water to remove HCl and the residual NO_x is absorbed on Union Carbide Corporation's Pura Siv N. The residual gas, containing less than about 20 ppm NO_x values, is discharged to the atmosphere.

Both compressor and tail gas cleanup requirements for this process are estimated to be about the same for production of 1000 tons per day of alumina as for the production of only about 75 tons per day of HNO_3 in ammonia-oxidation nitric acid plants. The requirements are small in comparison to modern commercial plants.

Chlorides

Chlorides enter the system with the calcined clay, process water makeup, and ammonia for acid makeup. They have been found to concentrate in the crystallization bleed stream with high efficiency and are expected to convert to HCl vapor during purge decomposition.

HCl has a high escaping tendency in 55% to 57% nitric acid solutions. Published experimental data (1) show that the molar distribution ratio, Y/X, is about 10 at 100°F, increases with temperature, and is independent of X at low concentrations. Thus HCl will be stripped to the gas phase during NO_x reconstitution and can be absorbed from the tail gas with water or dilute nitric acid solutions. It is then oxidized to Cl_2 with ozone, and the Cl_2 is absorbed in sodium hydroxide for disposal. Since HCl recycle in the acid is controlled, significant corrosion problems due to chloride ion are not expected in the Reynolds process.

Construction Materials

Construction materials for handling aluminum nitrates and nitric acid are well known, widely used, and commercially available. Selection of materials is based upon the knowledge that the resistance to corrosion by nitric acid is a direct function of chromium content so long as the carbon content is kept low to avoid the precipitation of chromium carbide. Thus for holding and containment operations of nitric acid solutions below the normal boiling point, S.S. 304L is satisfactory and use of the more expensive S.S. 316 provides no advantage. At temperatures between the normal boiling point and about 135°C a malleable 25% Cr, 1 Mo alloy, also highly resistant to chloride-induced stress corrosion cracking, is available for sheet, tube, etc. and a castable 26% Cr alloy is used for pumps and valves.

Heat transfer surfaces used for melting and boiling aluminum nitrate liquors and condensing nitric acid solutions at the boiling point require titanium. More exotic metals such as zirconium or tantalum are not required. In the fluid bed decomposers, wherein the vapors are produced and maintained above their dewpoint, metals are selected for their oxidation resistance. S.S. 304L has provided excellent service at 750°F for many years. At 1400°F (760°C), however, a higher oxidation resistance is desirable such as is provided by modern power plant boiler tubes or if desired by flame sprayed alumina coatings.

Gaskets, packing, etc. are made from fluorocarbon polymers. These are inert to nitrates and nitric acid, have satisfactorily low weep rates in thick section, and have sufficient thermal stability. Other plastics materials are subject to oxidation.

As with any acid process, all process streams comprising acidic liquors must be enclosed to prevent excessive corrosion of plant structures, regardless of environmental considerations. These enclosures would be vented to acid recovery to recover nitrate and avoid escape of corrosive vapors.

Energy Requirements

Fossil fuel specifications of 150,000 BTU per gallon ($42\ GJ/m^3$) fuel oil and 11,400 BTU/lb (26.5 GJ/tne) coal were used to calculate coal and oil consumption. An arbitrary assumption of 75% efficiency for coal combustion has been used for this paper so that detailed discussion of heat recovery assumptions and operations would not be required.

Figure 1 shows estimated values for the thermal energy input, solely to the process stream, required to carry out the required physical and chemical transformations, exclusive of any radiation and convection heat losses or inefficiencies due to steam condensate production or fuel combustion. Thus the values are free of many assumptions which frequently differ between different estimators.

After allowance for the indicated recovered and recycled heat, 17 mm BTU must be supplied to the process streams from steam or combustion of fuels. Of this, 0.48 mm BTU is required for product calcination and must be supplied by burning fuel oil at high temperature. It has been estimated that this heat input would require combustion of 9 gallons of fuel oil per ton, equivalent to 1.35 mm BTU, and that 0.71 mm BTU could be recovered from the hot flue gases and used to reduce the remaining process heat input requirement from 16.52 to 15.81 mm BTU per ton alumina. An additional 1 mm BTU has been estimated for non-process needs, run-off evaporation, and other environmental cleanup operations and 1 mm BTU has been allowed for radiation and convection losses, to give a total process heat input of 17.81 mm BTU to be supplied by combustion of coal. Purchased electrical energy is estimated to be 600 kwh/ton. This data is summarized in Table I.

Table I. Energy and Fossil Fuel Requirements

	Per Ton Alumina			Per Tne	
	mm BTU			Gj	
	Net	Gross	Fuel	Gross	Fuel
Fuel Oil	0.48	1.35	9.0 Gal.	1.57	37.4 L
Coal	17.81	23.75	1.04 Tons	27.64	1.04 Tne
Total Fuel Heat		25.10		29.21	
Purchased Power	600 KW	6.00*	0.26 Tons	6.98	.26 Tne
Total Fossil Fuel Impact		31.1 mm BTU 9.0 Gal. Fuel Oil 1.30 Tons Coal		36.2 Gj 37.4 L Fuel Oil 1.30 Tne Coal	

(*10,000 BTU heat rate assumed for modern power plant with full environmental controls)

Water Balance

The estimated water balance for the Reynolds process is presented in Table II. It has been assumed that boiler water blowdown will be used as cooling tower makeup and the cooling tower blowdown will be treated to recover process water and solids to be discarded. Area spillage and runoff would be evaporated and distilled to recover concentrated nitrates for recycle, and process water.

Estimated net potable and process water makeup is 1488 tons/day and cooling tower plus SO_x scrubber makeup is 11,160 tons/day. Total water requirement is 12,647 tons/day, equivalent to 2100 G.P.M. or 3700 acre-ft. per year. Eighty percent of this is exhausted to the atmosphere as cooling tower evaporation and windage. Only 15% is discarded as liquid wastes.

Table II. Estimated Water Balance

Basis: 1,000 tons alumina/day

Stream		Tons/Day	GPM
Input to Process Operations			
Water in ore		1,100	183
Water to leach residue wash		3,147	525
Water to wash iron removal residue		243	40.4
Make up to steam boilers		510	84.8
Make up to cooling tower		10,585	1,760
Make up to SO_x scrubbers		974	162
Miscellaneous, potable, etc.		100	16.6
	Total	16,672	2,771
Recovered from Process Operations			
Condensate from crystallization		1,950	324
Boiler water blowdown		400	66.5
Process area spillage and runoff		125	20.8
Cooling tower blowdown		450	74.8
	Total	2,925	486.2
Exhaust to Atmosphere			
Water from ore calcination		1,100	183
Acid recovery tailgas		5	0.8
Calciner off-gas		40	6.6
Cooling tower evaporation and windage		10,160	1,689
SO_x scrubber off gas		587	97.6
	Total	11,892	1,977
Effluent Wastes			
Water in leach residue		1,157	192
Water in iron removal sludge		123	20.4
SO_x scrubbing sludge		387	64.3
Miscellaneous		184	30.6
	Total	1,851	307.7
Net Water Makeup Required			
Process and potable		1,488	247
Cooling tower and SO_x scrubber		11,160	1,855
	Total	12,647	2,102

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