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THE ALUM-AMINE PROCESS FOR THE RECOVERY OF ALUMINA FROM SHALE

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THE ALUM-AMINE PROCESS FOR THE RECOVERY OF ALUMINA FROM SHALE

by

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ABSTRACT

This report describes laboratory experiments done to recover cell-grade alumina from aluminiferous shale.

The shale was baked with concentrated sulphuric acid to sulphate the aluminum, iron and potassium constituents and to render the silica insoluble. The sulphated shale was then leached with hot mother liquor which contained potassium sulphate. When the hot liquor was cooled, potassium alum was precipitated, thus bringing about an initial separation of the aluminum from the iron.

The potassium alum precipitate was purified either by recrystallization or by a treatment with a kerosene solution of Primene. Both of these treatments effectively reduced the level of iron contamination to the point that, when the purified alum was thermally decomposed and leached, the level of impurities in the alumina was sufficiently low for the material to meet the specifications for cell-grade alumina.

During the leaching of the decomposed alum, the potassium sulphate added initially to the circuit was recovered, together with the potassium originally present in the shale. As a result, by-product potassium sulphate should be recoverable from this type of processing.

The iron originally present in the shale was not recovered in a usable form. However, a major part of the sulphuric acid used initially in sulphating the shale should be recoverable from the off-gases produced during the decomposition of the alum.

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INTRODUCTION

At the present time, the aluminum industry in Canada is entirely dependent on imported alumina and bauxite for the production of aluminum. The same is true for a large segment of the aluminum industry in the United States.

To decrease this dependence upon outside sources for raw material for the aluminum industry, many attempts[1-20] have been made to utilize the enormous resources of clays and shales in Canada and the United States. These attempts, for the most part, have been unsuccessful because good imported bauxites are readily available, shipping charges by boat are moderate, and the costs of processing bauxite to high grade alumina by the Bayer method are reasonable. In contrast, since domestic clays and shales contain comparatively small amounts of aluminum and relatively large amounts of silicon and iron, the processing of the clays and shales to obtain alumina is expensive,[1,4,5,15] and many of the methods that have been tried have failed to produce a material which would meet the silica and iron specifications for cell-grade alumina.

With the recent resurgence in Canada, and in the United States, of attempts to recover cell-grade alumina from clays and shales, the Mines Branch undertook to review certain processes that had been tried with marginal success, and to determine by laboratory research whether any of these processes might be adapted to current needs in the light of our present technology. In particular, it seemed quite possible that some recent developments

in organic chemistry, relating to uranium technology, might be utilized for the removal of the last traces of iron from intermediate products, to permit the attainment of a satisfactory grade of alumina.

Although there are many clay and shale deposits throughout Canada, all of the experimental work reported herein was done on material from a large eastern Canadian deposit. A substantial amount of this shale was baked with concentrated sulphuric acid at the Mines Branch, to sulphate its various constituents. In essence, then, the problem resolved itself into one of recovering cell-grade alumina from a sulphated shale containing soluble sulphates of: aluminum, iron, titanium, magnesium, calcium, sodium and potassium.

EXPERIMENTAL PROCEDURE AND RESULTS

Chemical and Mineralogical Analyses of Shales and Sulphated Shale

The chemical analysis of the raw shale used in this investigation is shown under the heading Sample 1, in Table 1. For comparison, the analyses of some other Canadian clays and shales are also shown in the table.

TABLE 1

Chemical Analyses of Canadian Clays and Shales (%)

Constituent	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
SiO_2	58.20	59	60.1	61	60
Al_2O_3	23.01	33	20.1	25	20
Fe_2O_3	6.05	2	8.6	2.5	5.2
K_2O	3.45			1.3	
MgO	1.70	0.5	0.8	0.4	2.8
Na_2O	1.28			0.9	
C	1.25				
TiO_2	0.93				
CaO	0.80	0.3	4.3	0.4	3.6
S	0.14				
P_2O_5	0.09				
$K_2O + Na_2O$		1.9			2.4
L.O.I.	remainder				

Sample 1 – Eastern Canadian shale used in this project.

Sample 2 – Sample of a large British Columbia clay deposit[21,22]

Sample 3 – Average of several British Columbia clays and shales[22]

Sample 4 – Average of several Saskatchewan clays and shales[23]

Sample 5 – Average of several Quebec clays and shales[24]

Table 1 shows that the shale used in these experiments is not unique in its chemical composition but is typical of Canadian shales.

Based on the mineralogical and chemical analysis of

shale Sample 1, the approximate estimated composition of the raw

shale is as follows: quartz 35%, muscovite 32%, clay minerals 12%,

chlorite 11%, andalusite 6%, magnetite 2%, iron sulphides 1%, and

carbonaceous matter 1%. Of the above minerals, aluminum is present

in the muscovite, clay, chlorite and andalusite.

When shale Sample 1 was baked with an equal weight of

sulphuric acid, a sulphated shale was obtained. A partial analysis

of the sulphated shale is given in Table 2.

TABLE 2

Partial Analysis of Sulphated Shale

Constituent	Percent present in sulphated shale		Percent of constituent that is soluble[*]
	Total	Soluble[*]	
Al_2O_3	13.54	12.60	93
Fe_2O_3	3.82	3.61	95
K_2O	1.61	1.38	86
Na_2O	0.55	0.52	94

[*] Based on a finely ground 0.5 g sample leached in
100 ml of 0.5% v/v H_2SO_4 for 0.5 hr at $100^{\circ}C$.

By sulphation with concentrated H_2SO_4, 93% of the

aluminum in the shale was converted to sulphate which was soluble in

dilute acid. The other constituents (except silica) of the sulphated

shale are also readily soluble.

Preliminary Experiments

When sulphated shale was leached with a small amount

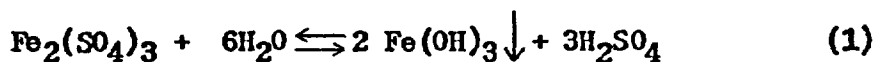of boiling water, a hot concentrated leach solution was obtained.

On cooling the solution, a viscous mass of aluminum sulphate was obtained which was difficult to filter. Washing of this mass to remove the large amount of entrained iron-bearing mother liquor from the crystals was very unsatisfactory, because of the slow filtration rate and the rapid dissolution of the gelatinous mass.

The difficulties encountered in the foregoing group of preliminary experiments were sufficient to show the desirability of developing a more satisfactory method of separating the aluminum sulphate from the iron-bearing leach liquor.

In the second group of preliminary experiments, an attempt was made to precipitate the iron from the concentrated leach liquor by the addition of alkali. It was found that large amounts of alkali were required, both because of the relatively large amount of iron in the solution and because of the inherent acidity of aluminum sulphate solutions.

A preferential separation of the iron from the aluminum could only be made by neutralization, in relatively dilute solutions. When concentrated solutions were used, large amounts of aluminum were precipitated with the iron.

In the third group of preliminary experiments, hydrolysis at elevated temperatures was tried as a method of decreasing the iron content of the leach liquor.

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2\,Fe(OH)_3 \downarrow + 3H_2SO_4 \qquad (1)$$

$$Fe_2(SO_4)_3 + 2H_2O \rightleftharpoons 2\,FeOHSO_4 \downarrow + H_2SO_4 \qquad (2)$$

In these experiments, sulphated shale was leached with distilled water for various periods of time at various temperatures, either in an autoclave or in open beakers. The slurries were filtered and washed, and the filtrates were analyzed. The results are given in Table 3. In additional hydrolysis experiments, a solution containing 12.8 g Al/1 and 3.0 g Fe/1 was obtained by leaching 50 g sulphated shale with 250 ml H_2O for 10 min at 95°C. The filtered leach solution was then hydrolyzed to form hydrolysis precipitates, either by heating in a reflux condenser at 106°C or by heating in a sealed glass tube at 100°C. The filtrates from these tests were analyzed chemically; the results are shown in Table 4. The hydrolysis precipitates were analyzed by X-ray diffraction.

TABLE 3

Hydrolysis of Sulphated Shale Slurries

Sulphated Shale (g)	Leach Water (ml)	Leach Temp (°C)	Leach Time (hr)	% Extraction	
				Al	Fe
50	1000	90	0.5	87	26
"	"	125	"	75	7
"	"	150	"	43	6
20	100	95	0.3	100	76
"	"	"	1.0	96	52
"	"	"	3.0	91	46
"	"	"	6.5	84	24

TABLE 4

Hydrolysis of Leach Solution

Reaction vessel	Hydrolysis		Filtrate pH	% Precipitation	
	Temp (^{o}C)	Time (hr)		Al	Fe
Reflux condenser	106	0.3	1.8		
	"	0.8	1.7		
	"	1.8	1.6		
	"	3.6	1.5		
	"	18.6	1.3	21	72
Sealed tube	100	63		56	93

From Table 3 it can be seen that, by hydrolysis, most of the iron dissolved from the shale could be precipitated (0.5 hr at $125^{o}C$), thus producing leach solutions that contain only small amounts of iron. However, complete removal of iron was not compatible with high extraction of aluminum. Table 4 shows that as the iron was precipitated by hydrolysis there was an increase in the acidity of the filtrate, in agreement with equations 1 and 2. By hydrolyzing for 63 hours, 93% of the iron in the leach liquor was precipitated, but there was also a precipitation of 56% of the aluminum.

Analysis of the hydrolysis precipitates by X-ray diffraction indicated the presence of jarosite, $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 4Fe(OH)_3$. The recognition of jarosite in the precipitate focussed attention on the high potassium content of the shale (see Table 1),

and initiated speculation on the effects that might be expected
if more potassium were present in the solutions.

From the data of Seidell[25] shown in Table 5, it was
evident that the solid phase in contact with saturated aluminum
sulphate solutions, containing potassium sulphate over a wide
range of concentrations, is the double salt, potassium aluminum
sulphate, $KAl(SO_4)_2 \cdot 12H_2O$.

TABLE 5

Solubility of K_2SO_4 in Aqueous Solutions of $Al_2(SO_4)_3$ at 25°C

g/100 g sat soln		Solid Phase
K_2SO_4	$Al_2(SO_4)_3$	
0.0	27.7	$Al_2(SO_4)_3 \cdot 18H_2O$
1.93	30.3	$Al_2(SO_4)_3 \cdot 18H_2O + KAl(SO_4)_2 \cdot 12H_2O$
1.94	27.9	$KAl(SO_4)_2 \cdot 12H_2O$
10.6	1.5	$KAl(SO_4)_2 \cdot 12H_2O$
11.5	1.4	$KAl(SO_4)_2 \cdot 12H_2O + K_2SO_4$
10.3	0.0	K_2SO_4

An examination of Tables 1 and 5 indicates that one of
the solid phases obtained by cooling hot concentrated leach solutions
from sulphated shale would consist of potassium aluminum sulphate.
This would be extremely desirable, since Partington[26] states
that potassium alum forms well-defined octahedral crystals which are
readily purified by recrystallization to give an alum that is free
from iron. Consequently, it was speculated that the complete
conversion of aluminum sulphate in leach solutions to potassium

alum, by the addition of the requisite amount of potassium sulphate, might be a useful intermediate step in the recovery of alumina from shale.

TABLE 6

Solubilities of Sulphates as a Function of Temperature

Temp (°C)	Wt Sulphate g per 100 g sat soln			$KAl(SO_4)_2 \cdot 12H_2O$ (g) per 100 g H_2O
	$Al_2(SO_4)_3$	K_2SO_4	$KAl(SO_4)_2 \cdot 12H_2O$	
20	27	10	10	11
80	42	18	63	321
85	-	-	74	-
90	45	19	-	2275
92.5	-	-	-	∞
100	47	19	-	-

Seidell[25], Table 6, also shows an interesting relationship between temperature and the solubilities of the various sulphates. The table indicates that recoveries of about 40% might be obtained, by cooling hot concentrated solutions of either aluminum sulphate or potassium sulphate. However, a mixture of these salts, in the form of potassium alum, is extremely soluble at high temperatures and, since potassium alum melts in its own water of hydration at 92.5°C, potassium alum recoveries of over 90% should be obtainable by cooling hot concentrated solutions.

To test this premise, a hot concentrated solution of aluminum sulphate, containing iron sulphate with a ratio of Al:Fe of 9:1, was prepared, and divided into two parts. After the

addition of potassium sulphate to one part, both solutions were

cooled and the crystals obtained were filtered and washed with

4 bed-volumes of water. The aluminum sulphate crystals, which were

difficult to wash, and which contained 30% of the iron from the

initial solution, had an Al:Fe ratio of 30:1. By comparison,

calculations showed that the coarse potassium alum crystals, which

were readily filtered and from which 98% of the iron in the liquor

was removed, had an Al:Fe ratio of about 400:1.

To demonstrate the applicability of alum formation to

the treatment of shale, a sample of sulphated shale, to which had

been added the requisite amount of potassium sulphate, was leached

with about an equal weight of water. The hot filtered leach

liquor, on cooling, formed potassium alum crystals which contained

only 0.12% Fe. By recrystallizing and washing the impure crystals

with equal amounts of water, potassium alum crystals were obtained

which contained only 0.003% Fe. Calculations show that alum

crystals of this purity would give, after decomposition and

leaching, an alumina product which would meet the cell-grade

specifications for iron.

When a search was made of the enormous volume of

literature on acid processes for the recovery of alumina [1-17],

it was found that certain processes utilizing alum [1,5,6,8-12,17]

had already been investigated, some of them on a pilot plant

scale [5,6,9-11,17]. The published results in some instances were

encouraging, but a few of the processes appeared to be cumbersome,

and the analyses of the alumina products only just met the

specifications for cell-grade alumina.

It seemed worthwhile, therefore, to investigate the alum approach more fully by experiments designed to determine whether it might be applied to the shale sample under study.

Leaching of Sulphated Shale

The first stage of the alum process to be investigated was the leaching of sulphated shale. For this purpose, a 2000 g sample of sulphated shale, to which 430 g K_2SO_4 was added for alum formation, was leached with 3300 ml H_2O for 30 min at 95°C. The slurry was filtered, and the hot filtered leach liquor was cooled and centrifuged to separate the alum crystals from the mother liquor. The filter residue was repulped twice with boiling water, filtered, and washed again with boiling water. The results are shown in Table 7.

TABLE 7

Recovery of Alum by Leaching Sulphated Shale with Water

Sample	Wt (g)	Vol (ml)	Al (g)	Fe (g)	Cum.% Extn.** Al	Fe
Head	2000		143.4[*] 133.4[**]	53.4[*] 50.4[**]		
Alum Crystals	1640		91.1	2.0	68.3	4.0
Mother Liquor		1560	11.2	29.8	76.7	63.1
1st wash		2850	19.2	1.1	91.1	65.3
2nd wash		6820	4.7	0.3	94.6	65.9
Residue	700		11.5			

[*] Based on % total Al and total Fe

[**] Based on % sol Al and sol Fe in 0.5% v/v H_2SO_4.

From Table 7, it is evident that about 77% of the soluble aluminum was extracted from the sulphated shale in the initial leaching stage. In this stage, the Al:Fe ratio was changed from 3:1 in the sulphated shale to 45:1 in the alum crystals, which contained 0.12% iron. These coarse crystals were considered suitable for further treatment for removal of iron.

An over-all extraction of about 95% of the aluminum was obtained when the residue was repulped and washed. The wash solutions, as shown in Table 7, contained a significant amount of aluminum, but only small amounts of iron. These wash solutions would be suitable for use, instead of fresh water, in the leaching of sulphated shale.

The mother liquors, from which potassium alum had been crystallized (Table 7), contained practically all of the extracted iron but only 8% of the total extracted aluminum. By discarding this mother liquor containing 19 g Fe/l, iron would be rejected from the circuit with the loss of only a comparatively small amount of aluminum. However, since this discard of liquor might be uneconomic and might create a disposal problem, methods of removing the iron from this liquor were sought.

To investigate the removal of iron from mother liquor, synthetic solutions were prepared which were saturated at room temperature with alum and contained 10-20 g Fe/l. To these solutions were added either increasing amounts of $CaCO_3$, or sufficient CaO to raise the pH to about 2 or 2.5. The mixtures were heated for 2.5 hr at 95°C to assist in the precipitation of iron by

neutralization and hydrolysis. The iron precipitates were removed by filtration. The results of these experiments are shown in Table 8.

From Table 8 it is evident that, by controlling conditions during the neutralization and hydrolysis, it was possible to remove about 80% of the iron and about 20% of the aluminum from synthetic mother liquors. Since mother liquors contain about 10% of the aluminum extracted from sulphated shale, a precipitation of 20% of the aluminum from the residual mother liquor corresponds to an over-all aluminum loss of only 2%. Hence, in an alumina recovery process, the treatment of mother liquor, prior to recycling it for leaching additional sulphated shale, removes most of the iron from the circuit with only a slight loss of aluminum. The iron precipitate, which contains jarosite, has been treated successfully, by thermal decomposition and leaching, for the recovery of potassium sulphate and an iron product.

To determine whether the iron removal treatment could be simplified by combining the separate stages of leaching and hydrolysis, additional experiments were done. Several 100 g samples of sulphated shale were treated at 95°C for various periods of time with 225 ml portions of a synthetic mother liquor. The hot slurries were filtered and the residues were each repulped and washed successively with 70, 35 and 35 ml portions of hot water. In another experiment, 50 g samples of sulphated shale were treated at 95°C for 2 hr with 70 ml portions of synthetic mother liquor containing about 10 or 20 g Fe/l. After filtering

TABLE 8

Treatment of Mother Liquor by Partial Neutralization and Hydrolysis

Mother Liquor				Reagent	Solution pH	Hydrolysis filtrate pH	% Extraction	
Vol (ml)	Al (g/l)	Fe (g/l)	pH				Al	Fe
50	9	20	1.45	0		1.2	0	14
"	"	"	"	1 g $CaCO_3$		1.30	7	77
"	"	"	"	2 g "		2.10	17	82
"	"	"	"	4 g "		2.85	72	94
"	"	"	"	8 g "		8.00	100	100
100	7	10	1.8	0.2 g CaO	2.0	1.6	2	37
"	"	"	"	1.1 g "	2.5	1.9	18	76
100	7	20	1.5	0.7 g CaO	2.0	1.4	5	42
"	"	"	"	1.8 g "	2.5	1.5	17	76

the hot slurries and washing each of the residues with two 10 ml

portions of hot water, potassium sulphate was added to the hot

leach liquor to promote alum formation. The results are shown in

Table 9.

TABLE 9

Leaching of Sulphated Shale with Mother Liquor at Elevated
Temperature to Combine Leaching and Hydrolysis

Mother Liquor 1		Leach Time (hr)	Filtration Time (hr)	Alum Crystals (%Fe)	Mother Liquor Fe (g/l)	% Extraction	
Al (g/l)	Fe (g/l)					Al	Fe
7	10.1	0.05	0.5			79	15
		1	0.5			90	−20[*]
		3	0.5			89	−56[*]
		8	0.5			88	−76[*]
6	9.9	2	0.5	0.11	7.5	86	−14[*]
6	20.5	2	0.5	0.22	12.9	89	−21[*]

[*] Percent removal from mother liquor 1.

From Table 9, it is evident that, by leaching sulphated

shale for a very short period of time with mother liquor, a 15%

extraction of iron from the shale was obtained. By using longer

leaching periods, to facilitate hydrolysis, there was no net

extraction of iron from the shale but, instead, there was a decrease

of from 14 to 76% of iron in the liquors. At the same time, all of

the aluminum in the recycled mother liquor was recovered, together

with 86 to 90% of the aluminum from the sulphated shale. These

data indicate that if sufficient alkali were used to neutralize
the acid generated by the hydrolysis of iron, a cyclic process,
under steady conditions, might be expected to produce:

(a) Mother liquors containing less than 10 g Fe/l.

(b) Alum crystals containing about 0.1% Fe.

(c) No net extraction of iron but, instead, the hydrolysis
     and rejection of iron with the shale residue.

(d) Recovery of about 90% of the soluble aluminum from
     the sulphated shale.

Purification of Alum Crystals

Impure alum crystals, obtained from the leaching of
sulphated shale and containing 0.12% Fe, were used in the
purification experiments. To minimize the amount of water required
for purifying the alum, a countercurrent crystallization technique,
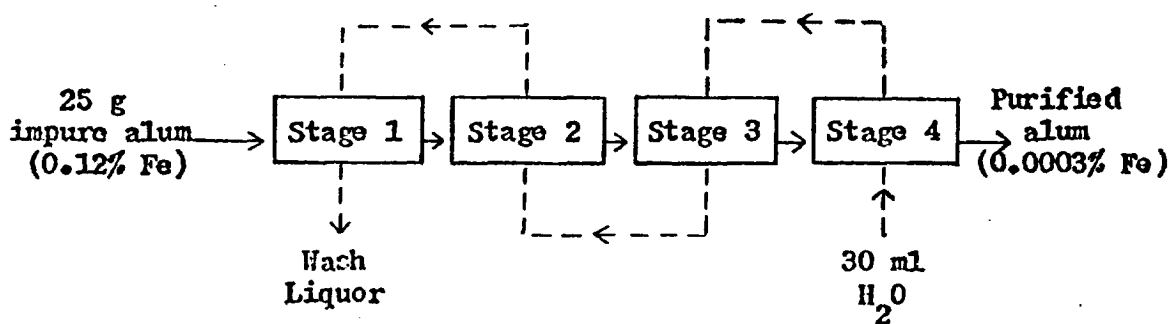as shown in Figure 1, was used.

Figure 1 - Countercurrent Crystallization of Alum.

In these experiments, 25 g of impure alum was used in each of the
four stages of crystallization. The slurries were heated to about
90°C, to dissolve the impure alum, and then cooled to crystallize
the purified alum. After filtration, the crystals and wash liquors
were moved countercurrently. These countercurrent crystallization
tests were continued until steady-state conditions were obtained,

then the crystals from the various stages were removed and analyzed.
The analytical data are shown in Table 10.

TABLE 10

Countercurrent Crystallization of Alum
(Steady-State Conditions)

Crystallization Stages	Wash Liquor (Fe g/1)	Alum Crystals (% Fe)
0		0.12
1	1.0	0.0100
2	0.06	0.0020
3	0.006	0.0005
4	0.001	0.0003

The countercurrent experiments show that two stages of
crystallization were sufficient to achieve adequate purification
to meet the requirements. Additional stages of crystallization
produced an alum of extremely high purity. The wash liquor from
these tests, because it was saturated with alum but low in iron,
would be suitable for leaching and washing of sulphated shale at
earlier stages in the circuit.

As an alternative to recrystallization, it was found
possible to use liquid-liquid extraction to remove iron. In an
experiment, 25 g of impure alum crystals in 25 ml of water was shaken,
in succession, with two 100 ml portions of a 5% v/v Primene JM[*]
solution in kerosene. The organic phase was decanted from the
aqueous slurry, and the crystals were separated from the aqueous
solution by filtration.

[*]Primene JM is a primary amine from Rohm & Haas.

TABLE 11

Purification of Alum by Liquid-Liquid Extraction

Primene stages	0	1	2
Alum purity (% Fe)	0.12	0.004	0.0005

The Primene solution effected an almost complete removal of iron from the alum crystals. The Primene solution, after treatment with alkali to precipitate iron, was suitable for recyoling. The aqueous solution which was separated from the purified alum orystals contained negligible amounts of iron and would be suitable for recyoling to form slurries with impure alum.

As shown by countercurrent liquid-liquid extraction tests by the Mines Branch Radioactivity Division, Primene solution removes mainly iron and only traces of aluminum. Under the steady-state conditions of one experiment, the aqueous phase was found to contain 0.002 g Fe/l and 50 g Al/l, whereas the organio phase contained 3.2 g Fe/l and 0.04 g Al/l. Other preliminary data from the countercurrent tests indicate a consumption of 3 to 4 lb CaO per lb iron, in the precipitation of iron from Primene; the Primene losses per lb iron extracted are 0.01-0.03 lb in the composite barren raffinate, 0.1-0.3 lb in the kerosene- or water-washed iron oxide cake, and 0.002 lb in the precipitation barren. The above data indicate that reagent costs should be low when Primene is used to remove the relatively small amounts of iron in the alum crystals.

Recovery of Alumina from Potassium Alum

The feasibility of preparing alumina from alum has already been established by the United States Bureau of Mines[9]. In this pilot-plant investigation[9], suitable stages in the process were found to be: dehydration of alum, at 375-475°C, in a vertical column flash dehydrator; decomposition of a mixture of anhydrous alum and 4% w/w petroleum coke, at temperatures up to 900°C, in a direct-fired rotary kiln; and leaching of potassium sulphate from the calcine, with hot or cold water, to yield a product which after heat stabilization treatment would be suitable as a cell feed in the production of aluminum.

A few tests were made in the Mines Branch laboratories to check the conditions for the recovery of alumina from alum. In some of these tests a fluidizer was used. It was a vertical 1 in. diameter silica tube, fitted at its base with a silica cloth for supporting the charge over the gas inlet. In these tests, either the entire charge was added initially to the fluidizer, which was then heated slowly, or the charge was added slowly to the preheated fluidizer (for flash decomposition) and then fluidization was continued for a given period of time. In other experiments, alum was dehydrated in an oven at 400°C and, after pulverization of the fragile porous mass, the powder was decomposed at various bed depths in a muffle furnace. All calcines were leached with water for the removal of potassium sulphate from the alumina. The data of Table 12 show that, under suitable conditions, the alum can be treated by decomposition and leaching to yield an alumina containing

only small amounts of potassium.

TABLE 12

Recovery of Alumina from Alum

Furnace	Temp (°C)	Bed Depth (cm)	Addition Time (hr)	Fluidizing or Decomposition Time (hr)	Potassium in Leached Alumina (%)
Fluidizer	715-900			3	0.42
"	750		0.5	1.5	0.24
"	900		0.8	0.5	0.13
Muffle	900-940	4		1	>5
"	900	1		1	0.21
"	900-940	0.5		1	0.08

Recovery of Alumina from Shale

Having prepared a suitable alumina from a pure alum, experiments were then begun to determine whether cell-grade alumina could be obtained from shale, by the process described in this report. For this purpose, three samples of sulphated shale, to which the requisite amount of potassium sulphate had been added, were leached at 95°C with hot water. The hot filtered leach liquors were cooled, and the resultant alum crystals were then separated from the mother liquor by a basket centrifuge or by a sintered glass filter funnel. The alum was crystallized and washed several times for the removal of iron, and the purified alum was decomposed at 900°C. By leaching the calcine with water for the removal of potassium sulphate, an alumina product was obtained. The purity of the alumina from these three tests is given in Table 13.

TABLE 13

Partial Analysis of Alumina Recovered from Sulphated Shale

Sample	Fe* (%)	K* (%)	Na* (%)	Si (%)	Cu (%)	Pb (%)	Mg (%)	Ni (%)	Ca (%)	Cr (%)	B (%)
1	0.09	0.04	n.d.	0.05	0.03	0.005	0.015		0.03	0.003	0.001
2	0.015	0.14	n.d.	0.08	0.04	0.02	0.01	0.004			0.001
3	0.005	0.18	n.d.		0.02	0.02	0.01	n.d.	n.d.	n.d.	

* Chemical analysis. The others are by semi-quantitative spectrographic analysis.

For comparison, the percentage impurities in typical Bayer aluminas are reported to be [1,3,4,7]: Fe, 0.01-0.03; K, 0.02; Na, 0.13-0.33; Si, 0.01-0.02; Mg, 0.01-0.03; Ca, 0.01-0.03; Ti, 0.002-0.005; P, 0.004. The average chemical composition of cell-grade alumina from the Kalunite alum process[6], which was used to produce electrolytic aluminum metal on a tonnage basis, is given as[7]: Fe, 0.06-0.10; K, 0.21-0.65; Na, n.d.; Si, 0.04-0.11; Ti, 0.003; P, 0.004-0.04; S, 0.13-0.76.

CONCLUSIONS

The foregoing experimental data show that alumina, of a grade acceptable for electric reduction to aluminum metal, can be prepared from this particular sample of low-grade aluminiferous shale. Although the work on this shale was done on laboratory scale only, enough information was obtained to warrant setting up small-scale closed-circuit pilot experiments.

A flow sheet for connecting the various steps suggested by these experiments has been sketched and is shown in Figure 2. Experiments based on this flow sheet are likely to yield sufficient information to determine whether additional large-scale pilot plant work is warranted.

Solids and Slurries
- - - Liquids and Gases

Sulphated Shale

LEACH,
HYDROLYZE, 95°C
FILTER

LEACH LIQUOR

K_2SO_4

CRYSTALLIZE, 25°C
FILTER

Mother Liquor

WASH, 95°C
FILTER

Shale
Residue

Impure Alum

Alternative
Purification
Processes

DISSOLVE, 90°C
CRYSTALLIZE, 25°C
FILTER

EXTRACTION
SEPARATION, 25°C

Organic
Phase

Aquoous Slurry

Make-Up
Amine   CaO

DISSOLVE, 90°C
CRYSTALLIZE, 25°C
FILTER

EXTRACTION
SEPARATION, 25°C

STRIPPING,
FILTRATION

Aquoous Slurry

Iron
Ppte

FILTER

Alum
Solution

Purified Alum

DEHYDRATE, 400°C H_2O

H_2SO_4

ACID
PLANT

SO_2
SO_3

DECOMPOSE, 900°C

LEACH, 95°C
FILTER

K_2SO_4 Solution

Wash Solution

WASH, 25°C
FILTER

CRYSTALLIZE, 25°C
FILTER

K_2SO_4

WASH, 25°C
FILTER

H_2O

STABILIZE, 1100°C

Cell-Grade
Alumina

Figure 2 - Flow Sheet for the Recovery of Alumina from Shale.

REFERENCES

1. J. D. Edwards, F. C. Frary and Z. Jeffries, The Aluminum
   Industry; Vol. 1, Aluminum and its Production, 358 pp.
   McGraw-Hill Book Co. Inc., New York, 1930.

2. G. S. Tilley, R. W. Millar and O. C. Ralston, Acid Processes
   for the Extraction of Alumina. U.S. Bureau of Mines,
   Bull. 267, 1-32 (1927).

3. J. H. Walthall, P. Miller and M. M. Striplin, Jr., Development
   of a Sulphuric Acid Process for Production of Alumina from
   Clay. Trans. Am. Inst. Chem. Engrs. 41, 53-140 (1945).

4. T. G. Pearson, The Chemical Background of the Aluminium
   Industry. Roy. Inst. Chem. Lectures, Monographs and
   Repts. No. 3, 103 pp (1955).

5. S. Weeks and H. B. McCoy, Materials Survey. Aluminum. Office
   Defence Mobilization, U.S. Dept. of Commerce (1956).

6. A. Fleischer, The Kalunite Process. Trans. Am. Inst. Mining
   Met. Engrs. 159, 267-79 (1944).

7. A. Fleischer and J. Glasser, Production of Aluminum from
   Kalunite Alumina. J. Metals 3, (Trans. 191), 634-6 (1951).

8. H. Pedersen, Production of Pure Alumina from Clay. Tids. Kemi
   Bergvaesen, 3, 161-4, 175-3 (1923); 4, 11-7, 55-6 (1924);
   Chem. Abstracts 18, 1882 (1924).

9. C. T. Baroch, A. W. Hackwood and P. G. Knickerbocker, Pilot
   Plant Investigations - Preparation of Alumina from
   Potassium Alum. U.S. Bureau of Mines, Rept. Invest. 3845,
   1-26 (1946).

10. C. C. Popoff, Cowlitz Clay Deposits near Castle Rock,
    Washington. U.S. Bureau of Mines, Rept. Invest. 5157,
    1-60 (1955).

11. W. R. Seyfried, The Ammonium Sulphate Process for the Extraction
    of Alumina from Clay and its Application in a Plant at
    Salem, Oregon. Am. Inst. Mining Met. Engrs., Mining Technology
    12, Tech. Pub. 2473, 12 pp (1948).

12. C. C. March, Investigations into Methods of Producing Pure
    Alumina from Kaolin by Sulphate Leaching. State College
    of Washington, Bull. E-4, 1-40 (1943).

13. R. C. Haff, Method of Recovering Alumina from Alumina-Bearing Ores. U.S. Pat. 2,551,944, Apr. 19, 1947.

14. O. Redlich, C. C. March, M. F. Adams, F. H. Sharp, E. Holt and J. Taylor, Extraction of Alumina from Clay. Ind. Eng. Chem. 38, 1181-7 (1946).

15. J. I. Hoffman, R. T. Leslie, H. J. Caul, L. J. Clark and J. D. Hoffman, Development of a Hydrochloric Acid Process for the Production of Alumina from Clay. J. Research Natl. Bur. Standards 37, 409-28 (1946). (Research Paper 1756)

16. H. Fulda and H. Ginsberg, Tonerde und Aluminum, Vol. i. W. DeGruyter & Co., Berlin, 1951.

17. H. W. St. Clair, S. F. Ravitz, A. T. Sweet and C. E. Plummer, The Ammonium Sulphate Process for Production of Alumina from Western Clays. Trans. Am. Inst. Mining Met. Engrs. 159, 255-66 (1944).

18. K. K. Kershner, C. W. Funk and W. A. Calhoun, Low Grade Bauxites and Clays as Potential Aluminum Resources. J. Metals 3, (Trans. AIME, 191), 1138-42 (1951).

19. T. P. Hignett, Production of Alumina from Clay by a Modified Pedersen Process. Ind. Eng. Chem. 39, No. 8, 1052-60 (1947).

20. F. R. Archibald and C. F. Jackson, Alumina from Clay by the Lime Sinter Method. Trans. Am. Inst. Mining Met. Engrs. 159, 227-38 (1944).

21. R. H. Beaton, Clayburn-Harbison Limited Operations in British Columbia. Trans. Can. Inst. Mining Met. 62, 22-5 (Bull. 52, No. 562, 90-3) (1959).

22. H. Ries and J. Keele, The Clay and Shale Deposits of the Western Provinces. Canada Dept. Mines, Geol. Survey Mem. 24-E, 231 pp (1921).

23. N. B. Davis, Report on The Clay Resources of Southern Saskatchewan. Canada Dept. Mines, Mines Branch Report 468, 89 pp (1918).

24. J. Keele, Clay and Shale Deposits of the Province of Quebec. Canada Dept. of Mines, Geol. Survey Mem. 64, 280 pp (1915).

25. A. Seidell, Solubilities of Inorganic and Metal Organic Compounds. 3rd Ed., Vol. 1, D. Van Nostrand Co. Inc., New York (1953).

26. J. R. Partington, A Text-book of Inorganic Chemistry. 6th Ed., Macmillan and Co. Limited, London (1950).