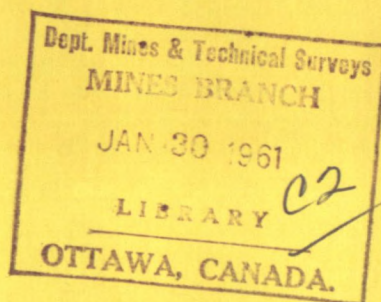




CANADA

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



DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

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The Development of the Alum-Amine Process for the Recovery of Alumina from Shale¹

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Based on a review of the extensive published literature on the recovery of alumina from clays and shale, sufficient experimental work was done on a bench scale to establish a flow sheet whereby these materials might be treated for the recovery of cell-grade alumina. The significant step in the processing is the recovery of potassium alum, and its purification by either recrystallization or liquid-liquid extraction.

In Canada, aluminum metal is produced from alumina recovered from bauxite. Since bauxite is found principally in tropical regions, it follows that the aluminum industry in Canada is totally dependent upon imported bauxite or alumina.

To decrease this dependence upon foreign materials, many attempts⁽¹⁻²⁰⁾ have been made to utilize the resources of clays and shales on this continent. None of the processes devised to date have succeeded in displacing the Bayer alumina process, but several of the processes have features which are of interest when assessed against the background of hydrometallurgical techniques developed in the last 15 years.

At the Mines Branch of the Department of Mines and Technical Surveys, various processes for producing alumina have been reviewed, and some of the better features from several have been combined with liquid-liquid extraction techniques into an integrated process for the production of cell-grade alumina. The chemical feasibility of the scheme has been investigated on a laboratory scale by the treatment of a Canadian shale.

The experimental work was done on a typical shale from a large eastern Canadian deposit. The chemical analysis of the raw shale is: 58.2% SiO₂, 23.0% Al₂O₃, 6.1% Fe₂O₃, 3.5% K₂O, 1.7% MgO, 1.3% Na₂O, 1.3% C, 0.9% TiO₂, 0.8% CaO, 0.1% S, 0.09% P₂O₅, and the remainder L.O.I. Based on the mineralogical and chemical analyses, the 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%.

Preliminary Experiments

When the shale was baked with an equal weight of concentrated H₂SO₄, a sulphated product was obtained from which 93% of the aluminum was extractable in 0.5% v/v H₂SO₄. The other constituents (except silica) of the sulphated shale are also soluble, e.g., 95% of the iron and 86% of the potassium.

When sulphated shale was leached with a small amount of 0.5% v/v H₂SO₄ and then filtered, a hot concentrated leach liquor was obtained. On cooling the liquor, a viscous crystalline mass of aluminum sulphate, with minor amounts of potassium alum, 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 unsatisfactory.

In contrast, by the addition of sufficient potassium sulphate to the hot concentrated leach liquor for the complete conversion of aluminum sulphate to potassium alum prior to cooling, well-defined, readily-filterable, octahedral crystals of potassium alum were formed which contained only 0.12% Fe. By recrystallizing and washing the impure crystals with equal weights of water, potassium alum crystals containing 0.003% Fe were obtained. Calculations show that alum crystals of this purity would give, after decomposition and leaching, an alumina product that would meet cell-grade specifications for iron.

It seemed worthwhile, therefore, to investigate the alum approach more fully by experiments designed to determine whether it could 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. K₂SO₄ was added for alum formation, was leached with 3300 ml. H₂O 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 1.

From Table 1, it is evident that about 77% of the soluble aluminum was extracted from the sulphated shale in the initial leaching. 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% Fe. An over-all extraction of about 95% of the soluble aluminum was obtained when the residue was repulped and washed. These wash solutions would be suitable for use, instead of fresh water, in the leaching of sulphated shale.

TABLE 1
RECOVERY OF ALUM
BY LEACHING SULPHATED SHALE WITH WATER

Sample	Wt (g)	Vol (ml)	Al (g)	Fe (g)	Cum. % Extn.*	
					Al	Fe
Head	2000		133.4*	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 % sol Al and sol Fe in 0.5% v/v H₂SO₄.

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Removal of Iron from Mother Liquor

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. Lime (CaO) was added to these solutions to raise the pH to 2.5. The mixtures were heated for 2.5 hr. at 95°C., to assist in the precipitation of iron by hydrolysis, and then the iron precipitates were removed by filtration. Under these conditions of 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 (see Table 1), a precipitation of 20% of the aluminum from mother liquor corresponds to an over-all aluminum loss of only 2%. When the iron precipitates, which contained hydrated iron oxides and jarosite, $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 4Fe(OH)_3$, were thermally decomposed and leached, potassium sulphate and an iron product were recovered.

To determine whether the iron removal treatment of mother liquors could be simplified by combining the separate stages of leaching and hydrolysis, several samples of sulphated shale were heated at 95°C. for various periods of time, with synthetic mother liquors containing 10 and 20 g. Fe/l. It was found that by leaching sulphated shale for about 10 minutes with mother liquor, a 15% extraction of iron from the shale was obtained. By using longer leaching periods, 1 to 8 hr. to facilitate hydrolysis, there was no net extraction of iron from the shale but 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. Hence, a combination leaching-hydrolysis stage for sulphated shale is possible for the extraction of aluminum into the liquor and the rejection of iron, by hydrolysis, into the shale residue.

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. Slurries of 1:1 mixtures of alum and water by weight 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 in a 4-stage countercurrent crystallization circuit. These tests were continued until steady-state conditions were obtained, and in the four successive stages the alum was found to contain, respectively, 0.01% Fe, 0.002% Fe, 0.0005% Fe, and 0.0003% Fe.

As an alternative to recrystallization, it was found possible to use liquid-liquid extraction to remove iron. Experimentally, an aqueous slurry of 25 g. of moist, freshly prepared impure alum crystals (0.12% Fe) in 25 ml. of water was shaken with 100 ml. of a 5% v/v Primene JM* solution in kerosene. The organic phase was decanted from the aqueous slurry, and the purified crystals which were separated from the aqueous solution by filtration contained 0.004% Fe. The purified alum crystals, after a second treatment with fresh water and fresh organic solution contained 0.0005% Fe. The Primene solution, therefore, effected an almost complete removal of iron from the alum.

As shown by countercurrent liquid-liquid extraction tests, 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 organic phase contained 3.2 g. Fe/l and 0.04 g. Al/l. Other preliminary results from the countercurrent tests indicate a consumption of 3 to 4 lb. CaO and 0.1 to 0.2 lb. Primene, per lb. iron removed from Primene, during the regeneration of Primene for recycling. These results indicate that reagent costs should be low when Primene is used to remove the relatively small amounts of iron in the alum crystals.

*Primene JM is a primary amine from the Rohm and Haas Company, Philadelphia 5, Penn., U.S.A.

FLOW SHEET FOR ALUMINA RECOVERY FROM SULPHATED SHALE

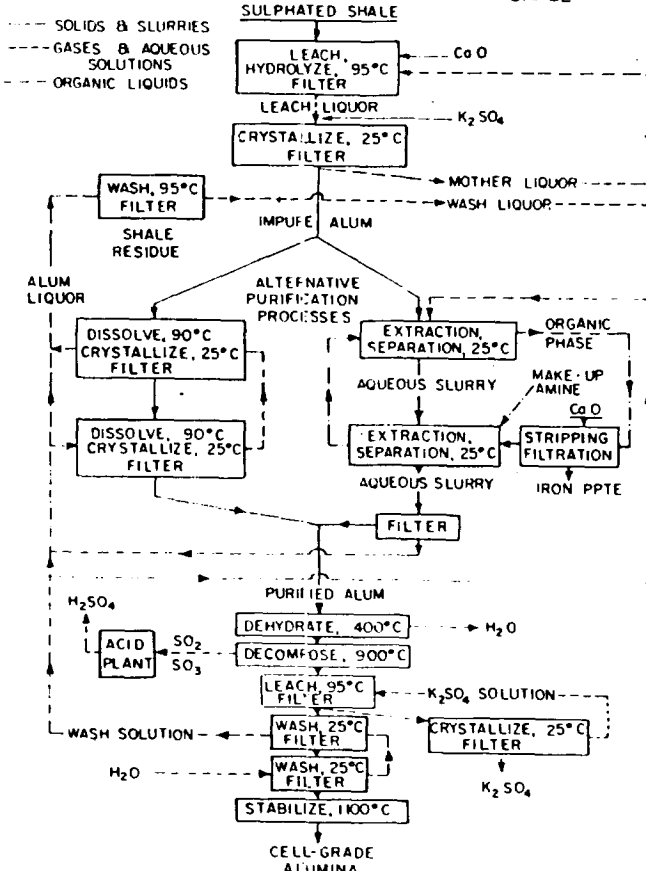


Figure 1—Flow sheet for alumina recovery from sulphated shale.

Recovery of Alumina from Alum

The feasibility of preparing alumina from alum has already been established in a pilot plant investigation in the United States⁽⁹⁾. In a few experiments at the Mines Branch laboratories at Ottawa, pure chemical grade alum was dehydrated in an oven at 400°C. and, after pulverization of the fragile porous mass, the powder was decomposed at about 900°C., at a shallow bed depth of 0.5 cm. in a muffle furnace. In other tests, alum was decomposed in a fluidizer, which consisted of a vertical 1 in. diameter silica tube, fitted at its base with a silica cloth for supporting the charge over the gas inlet. Alum was added slowly to the fluidizer at 900°C. for flash decomposition and brief fluidization. All calcines were then leached with water for the removal of potassium sulphate from the alumina. The results from these tests show that, under suitable conditions, the alum can be treated by decomposition and leaching to yield an alumina containing only small amounts of potassium, e.g., 0.08 - 0.13% K.

Recovery of Alumina from Shale

Having prepared a suitable alumina from pure alum, experiments were done to determine whether cell-grade alumina could be obtained from shale, by the foregoing process. 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 separated from the mother liquor by a basket centrifuge or by a sintered glass filter. The alum was recrystallized 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 tests is given in Table 2.

TABLE 2
PARTIAL ANALYSIS OF ALUMINA RECOVERED FROM SULPHATED SHALE

Sample	Fe (%)	K (%)	Na (%)	Si (%)	Cu (%)	Ti (%)	V (%)	Pb (%)	Mg (%)	Ni (%)	Ca (%)	Cr (%)	B (%)
1	0.09*	0.04*	nd*	0.05	0.03	0.001	<0.01	0.005	0.015	nd	0.03	0.003	0.001
2	0.015*	0.14*	nd*	0.08	0.04	0.001	<0.01	0.02	0.01	0.004	nd	nd	0.001
3	0.005*	0.18*	nd*	na	0.002*	0.04*	<0.01*	0.02	0.01	nd	nd	nd	na

*Chemical analysis. The others are by semi-quantitative spectrographic analysis.
nd None detected.
na Not available.

The purity of these alumina products compares favorably with Kalunite alumina from which commercially acceptable aluminum metal has been prepared⁽⁷⁾. The impurity level is slightly in excess of that obtained by the Bayer process, but some improvement might be expected if specific precautions were taken to keep the impurity level low.

A flow sheet for connecting the various steps suggested by these experiments has been sketched and is shown in Figure 1. The flow sheet was investigated by operating the process on a small-scale cyclic basis. In these cyclic tests, 100 g. samples of sulphated shale were leached at 95°C. for 1 hr. with 200 ml. of mother liquor and then with 200 ml. of wash liquor. By filtration, the leach solution was separated from the shale residue, which was washed first with 150 ml. of alum liquor and then with 50 ml. of fresh water. The hot filtered leach liquor, to which was added about 20 g. K_2SO_4 , was cooled at 25°C. to form impure alum crystals and mother liquor.

In the cyclic tests, about 94% of the soluble aluminum from the sulphated shale was recovered in the form of impure alum crystals. These alum crystals contained about 0.2% Fe. In subsequent cycles, the accumulation of sulphuric acid from the hydrolysis of ferric sulphate gradually decreased the extent of hydrolysis so that the recycle mother liquor and the alum crystals contained increasing amounts of iron. However, by the addition of CaO to the leaching stage, for neutralizing the acid and thereby permitting continued hydrolysis of iron from the liquor, alum crystals of low iron content were again obtained. The impure alum crystals were purified by the use of equal weights of water in a 5-stage countercurrent crystallization circuit. A spectrographic analysis of products indicated the removal, from the crude alum crystals, of not only iron but also sodium, magnesium, calcium, titanium, and smaller amounts of other contaminants.

The purified alum crystals were dehydrated in silica trays at 400°C. and decomposed at 900°C. with the off-gases being vented to the atmosphere. The decomposed alum was leached at 95°C. and washed at 25°C. for the removal of potassium sulphate from the alumina. The cold wash solution was used in the crystallization circuit for the purification of crude alum. The hot leach solution from the leaching of decomposed alum, after cooling and filtering to remove K_2SO_4 crystals, was reheated and recycled for leaching additional K_2SO_4 . The K_2SO_4 crystals were recycled to the head of the circuit to form alum. Alumina from the cyclic tests was of a purity comparable to that in Table 2. Additional experimental investigations based on the flow sheet are now in progress, to determine whether large-scale pilot plant work is warranted. Any final judgment as to the relative merits of this method of producing alumina will have to await an economic assessment based on pilot plant data.

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