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ACID EXTRACTION OF ALUMINA FROM CANADIAN NON-BAUXITE SOURCES AT CANMET

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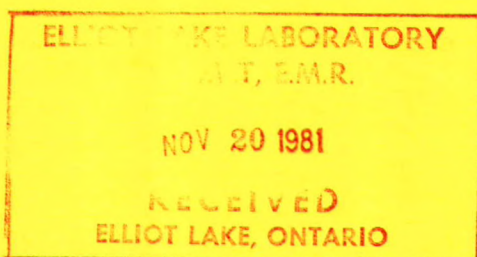
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Errata sheet for CANMET Report 81-2E – ACID EXTRACTION OF ALUMINA FROM CANADIAN NON-BAUXITE SOURCES AT CANMET by C. Hamer

Table 5, page 11 has been corrected.

Table 5 – Alumina by the hydrochloric acid-gas sparge process average of 10 leach cycles, ug/g

Element	Target	1st crystallization	2nd crystallization	Water leached calcine
Fe	200	>1000	42	24
Si	115	84	52	60
Mg	12	>1000	102	14
Ca	600	430	37	na
Cr	12	121	35	22
V	11	107	6	na
Na	3000	<1000	<1000	na
Mn	12	18	<8	na
Zn	160	27	<25	na
Ti	30	37	5	na
P	4	na	na	35*
K	40	52**	na	<6**

na – not analyzed

* – average 5 samples

** – one sample

ACID EXTRACTION OF ALUMINA FROM CANADIAN NON-BAUXITE SOURCES AT CANMET

by

C. Hamer*

ABSTRACT

CANMET's laboratory work on acid extraction processes for the recovery of alumina from Canadian non-bauxite sources is reviewed. The materials investigated were anorthosite, clays and coal waste.

Several processes were used to improve the acid solubility of anorthosite. In one method the rock was melted and quenched as an amorphous glass; more than 95% of the aluminum content was extracted from this material in mineral acids. In another process the extraction of aluminum by hydrochloric acid leaching of finely ground anorthosite was greatly increased - from 30% to over 80% - by adding to the leach a small amount of fluosilicic acid. It was also found that anorthosites from some deposits were soluble in hydrochloric acid without fluosilicic acid; this material approached the composition of bytownite and was composed of unaltered feldspar.

Six Canadian clays were examined as alumina sources. The after calcining at temperatures of between 750 and 850°C, alumina contents ranged from 23 to 29%. Material from one deposit was upgraded by wet screening to remove coarse quartz and produced a 36% Al_2O_3 calcine. Aluminum extraction in either hydrochloric or sulphuric acid was in the 85 to 90% range for all samples.

Waste coal from the Hat Creek, B.C. deposit was also examined as a source of alumina. The material was burned in a fluid-bed combustor at 750 to 850°C to produce an acid soluble ash containing 30.8% Al_2O_3. Aluminum extraction of 80% was achieved in a 30-min leach in 26 m % HCl.

Alumina was recovered from hydrochloric acid leachates by sparging with HCl gas to crystallize aluminum trichloride hexahydrate. The crystals were dissolved and recrystallized to purify the product prior to calcining to alumina. It often contained impurities - P, Mg and Cr - in excess of the specifications for cell-grade material. To overcome this problem a process was developed wherein the hydrochloric acid leachate was evaporated and calcined at 400°C to produce a crude alumina. After water leaching to remove soluble chlorides, this material was treated by a modified Bayer process to produce alumina which met cell-grade specifications.

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EXTRACTION À L'ACIDE DE L'ALUMINE DES SOURCES NON-BAUXITIQUES CANADIENNES AU CANMET

par

C. Hamer*

RÉSUMÉ

Le travail effectué dans les laboratoires du CANMET sur les procédés d'extraction à l'acide pour la récupération de l'alumine des sources non-bauxitiques canadiennes est passé en revue. Les matières étudiées sont l'anorthosite, les argiles et les résidus du charbon.

Plusieurs procédés ont été employés pour améliorer la solubilité à l'acide de l'anorthosite. Dans une des méthodes, la pierre a été fusionnée et éteinte pour former un verre amorphe; plus de 95% de sa teneur en aluminium a été extraite dans des acides minéraux. Dans un autre procédé, l'extraction de l'alumine par la lixiviation à l'acide chlorhydrique de l'anorthosite finement moulu s'est grandement accrue - de 30% à plus de 80% - en ajoutant une petite quantité d'acide fluosilicique à la solution de lixiviation. On a aussi découvert que les anorthosites provenant de certains gisements étaient solubles dans l'acide chlorhydrique sans avoir à y ajouter d'acide fluosilicique; la composition de cette matière ressemble à celle du bytownite et elle est formée de feldspath non-modifié.

Six argiles canadiennes ont été examinées comme sources d'alumine. Après la calcination à des températures entre 750 et 850°C, la teneur d'alumine pouvait variée entre 23 et 29%. Un matériau provenant d'un des dépôts a été enrichi par criblage humide pour enlever le quartz grossier et a donné un produit calciné, Al_2O_3, à 36%. L'extraction de l'aluminium dans l'acide chlorhydrique ou dans l'acide sulfurique a été de 85 à 90% pour tous les échantillons.

Les résidus du charbon provenant d'un gisement de Hat Creek (C.-B.) ont aussi été examinés comme source possible d'alumine. Le matériau a été brûlé dans un four de combustion par lit fluidisé à des températures de 750 à 850°C pour obtenir une cendre soluble dans l'acide et contenant 30.8% de Al_2O_3. Une extraction de l'aluminium de 80% a été réalisée avec une lixiviation de 30 minutes dans du HCl à 26 m %.

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L'alumine a été récupérée des produits de lixiviation à l'acide chlorhydrique par aspersion avec du gaz HCl pour cristalliser l'hexahydrate de trichlorure d'aluminium. Les cristaux ont été dissous et recristallisé pour purifier le produit avant de le calciner en alumine. Celui-ci contenait très souvent des impuretés - P, Mg et Cr - au-delà des normes établies pour les matériaux de piles. Afin de surmonter ce problème, un procédé a été mis au point selon lequel le produit de lixiviation à l'acide chlorhydrique est évaporé et calciné à 400°C pour produire l'alumine brut. Après la lixiviation à l'eau pour enlever les chlorures solubles, ce matériau a été traité selon un procédé de Bayer modifié pour produire de l'alumine qui rencontre les normes de qualité requises dans les piles.

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INTRODUCTION

Although Canada is one of the world's major aluminum producers, it has no domestic source of bauxite, the commercial ore of aluminum. Bauxite, an impure hydrated aluminum oxide containing approximately 50% Al_2O_3, accounts for only a small portion of the aluminum in the earth's crust. Most aluminum is associated with feldspars, clays, shales, etc., as aluminum silicates and it is these minerals which, for economic or strategic reasons, may become aluminum ore in the future.

CANMET initiated a project in 1975 – Alumina from Non-Bauxite Sources – the objectives of which were to evaluate potential domestic non-bauxite alumina sources, and to investigate and develop technology for the recovery of alumina from these sources. Potential sources are considered to be anorthosite, clay, nepheline syenite and coal associated materials which will be described in detail by others in a future report. The technologies for extracting alumina from raw materials can be classified as either alkaline sinter or acid processes. This report will review CANMET's laboratory work on acid extraction processes from anorthosite, clay and coal associated materials. Detailed descriptions of the experimental work can be found in the references to Division Laboratory reports made throughout the text.

ANORTHOSITE

Anorthosite was the first of the possible Canadian non-bauxite alumina sources to be investigated at CANMET, principally because the eastern section of the Canadian Shield contains the world's largest concentration of this rock. Anorthosite is an igneous rock containing at least 90% plagioclase feldspar (1). The chemical composition of plagioclase is a continuous series between $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. By definition, anorthosite contains between 17.6% Al_2O_3 (90% albite) and 36.7% Al_2O_3 (100% anorthite). The anorthosites of interest usually have an alumina content of 28% to 33% if pure and range between labradorite, An 50, and bytownite, An 80.

Initial test work was done on a sample from a deposit at Lac St. Jean in Quebec, next to Canada's largest aluminum complex at Arvida. This material was used in studies of various acid processes – melt-quench, hydrochemical, lime and lime-soda sinter, and hydrochloric acid-fluosilicic acid. Ensuing samples came from 11 deposits in Ontario, 6 in Quebec and 2 in Newfoundland. Those from Harp Lake, Labrador and Shawmere, Ontario were found amenable to acid leaching. Table 1 gives the chemical composition of the anorthosites used in this project.

ACID EXTRACTION OF ALUMINA FROM MELTED AND QUENCHED ANORTHOSITE

Most anorthosites are slightly soluble in acid and at the time the project began it was thought that all were acid insoluble. One approach to rendering the aluminum acid soluble is to destroy the crystalline structure of the anorthosite. This was accomplished by raising the temperature of the rock above its melting point between 1500 and 1540°C and pouring it at 1600 to 1640°C into cast iron chill molds. The resultant glass-like material was completely amorphous. It fractured on quenching and was further crushed to minus 300 um for leaching tests (2).

Leach tests were conducted on melted and quenched anorthosite from Lac St. Jean with sulphuric, hydrochloric and nitric acids of various

Table 1 – Analyses of Canadian anorthosites (*m* %)

	Lac St. Jean	Harp Lake	Shawmere
Al_2O_3	27.0	30.6	34.0
SiO_2	53.1	48.9	44.9
Fe_2O_3	2.31	0.73	2.24
CaO	10.6	14.4	14.7
Na_2O	4.97	2.80	2.30
K_2O	0.53	0.30	0.11
MgO	0.31	1.00	1.69
TiO_2	0.12	0.18	<0.05

concentrations and quantities. Although some tests were conducted at lower temperatures, most were done at or near the reflux boiling temperatures of the acids, the higher temperature resulting in better extraction. The extraction of aluminum was 95% in 30-min leaches with a minimum of either 10 m % sulphuric or hydrochloric acids. Nitric acid concentrations of 30 m % were required to approach 95% extraction, Fig. 1. It was found that extraction was essentially complete in a 15-min leach. The optimum quantity of acid appeared to be 105% to 110% of the stoichiometric amount required to react with aluminum and the soluble impurities. The other principal constituents of the anorthosite – CaO, Na_2O and Fe_2O_3 – were extracted with equal ease, thus producing a severely contaminated leachate.

Attempts were made to separate iron from the melted and quenched product. During melting
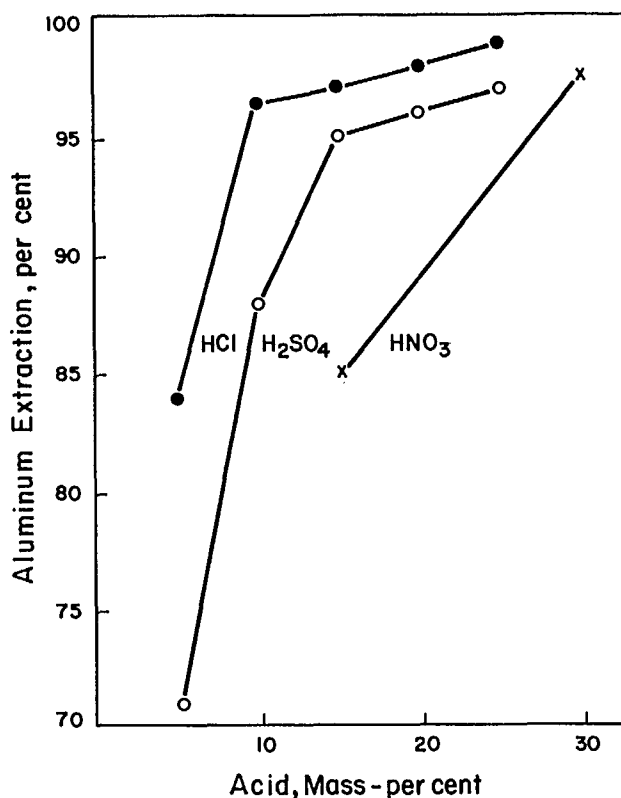
Fig. 1 – Effect of acid concentration on aluminum extraction from melted and quenched anorthosite, 30 min leach, reflux boiling temperature

the iron oxides were reduced to metallic shot by the graphite crucible, or by adding carbon. However, the iron shot was too small and the melt too viscous to achieve gravity separation in the crucible. Approximately 50% of the iron could be removed from the crushed sample with a hand magnet with a loss of about 5% of the total aluminum content.

Because of the high electric power consumption required to melt anorthosite rock, it was determined that this was not a feasible approach for extracting aluminum.

EXTRACTION OF ALUMINUM FROM ANORTHOSITE BY HCl-H_2SiF_6 LEACHING

Laboratory investigations were conducted to determine the feasibility of utilizing the aggressive nature of the fluoride ion, i.e., fluosilicic acid in association with a mineral acid to disrupt the crystal structure of anorthosite and thus allow leaching of aluminum to take place (3,4). The effects of the various leaching parameters of time, temperature, acid concentration and quantity, and feed particle size were determined. Extraction tests were conducted in a Teflon beaker fitted with a Teflon condenser. The leaches were stirred. With the exception of experiments to determine the effects of raw material particle size, minus 45-μm material was used. To overcome a tendency of the leach to foam when the finely ground feed was added to hot acid, the feed was added to cold acid and then heated. All leaches were made with 26 m % hydrochloric acid (296 g/L) in an amount equal to 115% of the stoichiometric amount required to convert all the soluble compounds to their respective chlorides. Fluosilicic acid was added to the leaches in amounts to give ratios of between 0.013 and 0.185 H_2SiF_6:1.0 HCl.

In 26 m % hydrochloric acid, extraction from minus 45-μm Lac St. Jean anorthosite was 31% in a 2-h leach, increasing slowly to 54% in a 7-h leach. The effect of adding fluosilicic acid to the HCl leach was quite dramatic as shown in Fig. 2. In a 2-h leach the aluminum extraction increased to 84% using a mass ratio of 0.14 H_2SiF_6:1.0 HCl.

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Fig. 2 - Effect of the H_2SiF_6:HCl mass ratio on the extraction of aluminum from -45 um anorthosite with 26 m % HCl, 2-h leach, 108°C

Calcium and sodium were also extracted in the fluoride-assisted leach; calcium extraction being slightly higher than aluminum and sodium slightl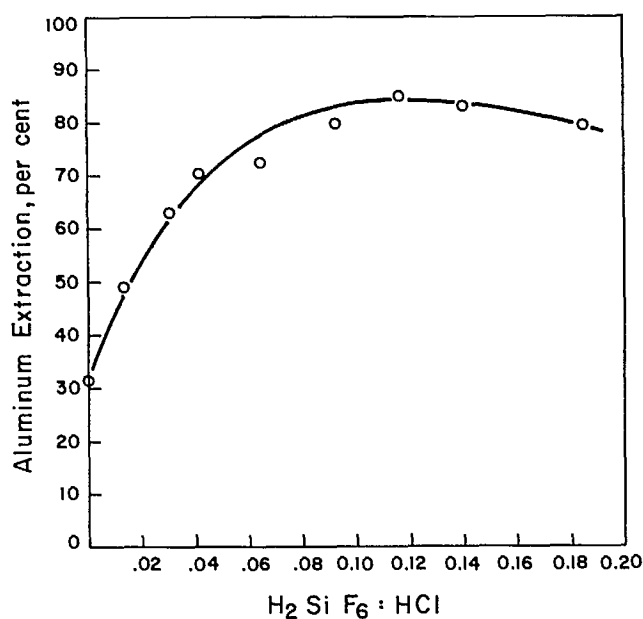y lower. To confirm the apparent differences in solubilities between the sodium- and calcium-rich ends of the plagioclase series, a sample of andesine (An 30-50) and of bytownite (An 70-90) were leached with a very small addition of H_2SiF_6 (0.013 ratio). In a 4-h leach aluminum extractions were 17% from the andesine, 61% from the Lac St. Jean anorthosite (labradorite An 50) and 77% from the bytownite. This indicated that the calcium-rich end of the plagioclase series was far more acid-soluble than the sodium rich end.

Although leaches were conducted with the addition of varying amounts of fluosilicic acid, the soluble silicon in the leachate was almost independent of the initial amount added. The silicon in solution was approximately 10^{-4} times the aluminum concentration.

Feed size was shown to have a major effect on aluminum extraction in the HCl-H_2SiF_6 leach. In a 4-h leach with 0.14 H_2SiF_6:1.0 HCl of sized feed material, aluminum extraction varied

from 28% for the minus 212-um size fraction to 91% for minus 45-um material. Fine grinding of anorthosite appeared essential for good aluminum extraction.

The role of the fluoride ion in promoting the extraction of aluminum is not clearly understood. It is postulated that aluminum, calcium and sodium are leached out of the matrix leaving a layer of amorphous silica adhering to the particles. The increasing thickness of silica retards the movement of ions so that the reaction is at least partially diffusion controlled. It is possible that the effect of the fluoride ion is to alter the nature of the silica layer in such a manner that its permeability is increased. Data from aluminum extraction versus leach duration were put in the form of a diffusion controlled shrinking core model. The resultant curves strongly support this model (Fig. 3).

EXTRACTION OF ALUMINUM FROM ANORTHOSITE BY HCl LEACHING

Subsequent to the foregoing extraction tests with HCl-H_2SiF_6, anorthosites from other deposits in Quebec and Ontario were examined. It was found that material from a few of these deposits was amenable to extraction with hydrochloric acid without requiring fluosilicic acid. These anorthosites approached the composition of bytownite and appeared to be composed of fresh unaltered feldspar. For example, in a 4-h leach of minus 45-um feed in 26 m % HCl, aluminum extractions of 85% to 90% were obtained from anorthosites of the Harp Lake, Labrador and Shawmere, Ontario deposits. Analyses of these samples are given in Table 1.

CLAYS AND SHALES

Much of Canada south of the Canadian Shield is covered with clay and shale but little of this material can be considered as a potential source of alumina. Most are of heterogeneous composition in terms of both clay minerals and non-clay minerals. The clay minerals contain kaolinite, illites, and montmorillonites whereas the
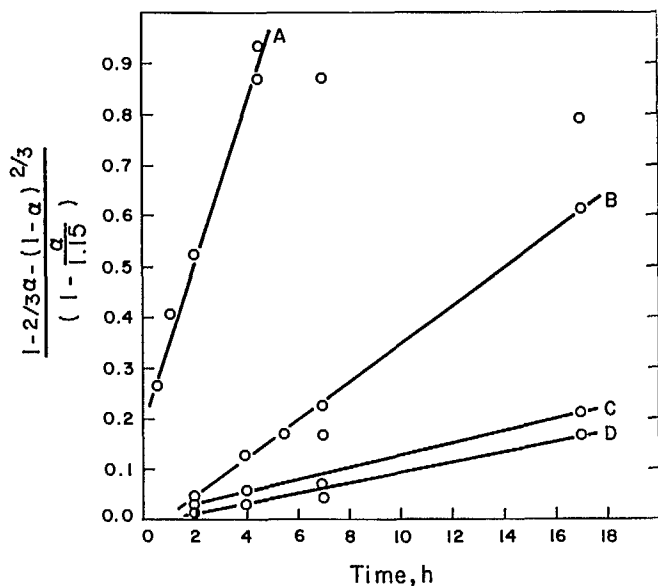
$$\frac{1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}}{(1 - \frac{\alpha}{1.15})}$$

Fig. 3 - Diffusion model correlation of data on aluminum extraction versus leach duration. α is the fraction of the anorthosite that has reacted

Curve A - minus 45 μm, 0.14 ratio

Curve B - minus 45 μm, 0.013 ratio

Curve C - minus 75 μm plus 45 μm, 0.14 ratio

Curve D - minus 75 μm plus 45 μm, 0.013 ratio

non-clay mineral is primarily quartz but often with some feldspar (5). Six clays were examined by Quon to determine their amenability to aluminum extraction (6,7,8). These originated in areas which appear to have the greatest potential as clay sources for alumina. They would require drilling and testing to establish quality and quantity but appear large enough at 50 to 100 Mt. Chemical analyses of the six samples are given in Table 2. The first five are from the Whitemud Formation in southern Saskatchewan and the last is from northern Ontario.

As shown in Table 2, the clays are generally of poor quality, i.e., with high SiO_2 and low Al_2O_3 contents relative to pure kaolin. The sample from Fir Mountain consisted mineralogically of 43% kaolin and 39% quartz with the remainder

being mica, goethite, siderite, feldspar, etc. As received, the sample contained 21% Al_2O_3, principaly as very fine grained kaolinitic sands. The quartz had larger grains much of which could be removed by wet screening through a 75-μm sieve. The minus 75-μm fraction was almost pure kaolin, analyzing 36.32% Al_2O_3 after calcining. Only the Fir Mountain sample exhibited this constituent size difference that permitted beneficiation by screening.

CALCINATION

The acid solubility of aluminum from clay is greatly enhanced by calcining. The calcining temperature and the soak time at temperature must be sufficient to dehydroxylate the clay, and yet not so extreme as to cause alumina and silica to combine as insoluble aluminosilicates. The effect of calcination temperature and soak times was determined over the range of 500 to 950°C and of soak times from 10 to 60 min. The optimum temperature range was 750 to 850°C and optimum soak time was 30 min at the lower temperature, decreasing to 10 min at the higher temperatures as determined by testing aluminum solubility of calcined clay in a standard acid leach.

ACID EXTRACTION OF ALUMINUM FROM CALCINED CLAY

The parameters affecting the acid extraction of aluminum from clays are: acid concentration, leach duration, leach temperature and feed size. To ensure homogeneity, samples were pulverized to minus 500 μm and blended. Hence feed material was quite fine and particle size was not studied as a variable in the experimental work. Essentially duplicate extraction tests were made in hydrochloric and sulphuric acids. A minor amount of work was done with nitric acid.

Figure 4 shows the effect of leach time on aluminum extraction in 26 m % HCl. The curves for extraction in 20 m % H_2SO_4 were similar. Acid was preheated to 90°C at which point the sample was added. The exothermic reaction between clay and acid caused the temperature to reach reflux boiling (105°C to 110°C) within a few minutes. Between 70% and 80% of the total aluminum content in the clay was extracted within the first 15 min

Table 2 - Analyses of clays calcined at 750°-850°C, m %

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Total
Fir Mountain*	36.32	61.02	1.00	0.11	0.15	0.075	0.09	1.45⁻	100.21
Willow Bunch A	24.76	68.84	2.17	0.25	0.48	0.45	0.36	1.08	98.39
Willow Bunch B	23.62	71.76	2.43	0.16	0.37	0.53	0.24	0.78	99.89
Willows C	31.86	66.33	2.02	0.08	0.22	0.15	0.67	1.01	102.34
Flintoft D	26.62	70.57	1.12	0.10	0.46	0.77	0.14	0.77	100.55
Smoky Falls S	29.04	64.33	5.01	0.11	0.19	0.30	0.08	1.11	100.7

*Beneficiated by wet screening 75 um
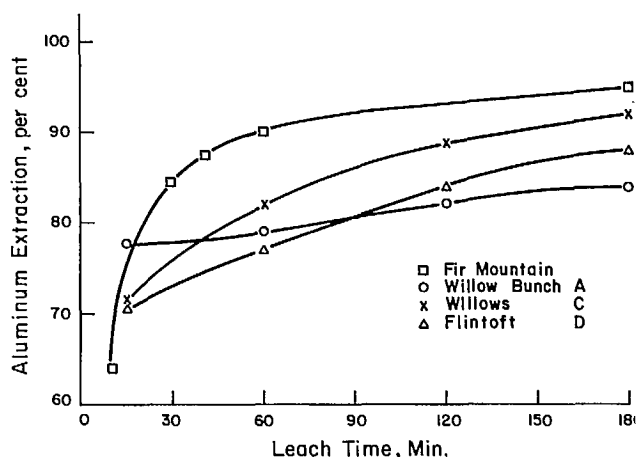
Fig. 4 - Effect of leach time on aluminum extraction from calcined clay in 26 m % HCl at 105°C

of leaching. Extraction increased slowly thereafter to 85 - 90% in either acid. The rapid initial aluminum extraction was due to the attack on the kaolin fraction of the clay. The slow extraction thereafter was due to leaching of the more inert aluminosilicates such as the micas and feldspars. The variation in extractions from different clays was attributable to the varying mineralogical constituents.

Most of the impurities associated with the clay were dissolved during leaching along with the aluminum. In 20 m % HCl, for example, a 2-h leach solubilized approximately 100% of the cal-

cium and sodium, 85% of the magnesium, 80% of the iron and 60% of the potassium. Silica appeared soluble to about 0.01%.

COAL-ASSOCIATED MATERIALS

Material associated with coal deposits can have relatively high aluminum contents. These are the clays and shales interbedded with the coal seams which are available as mine or washery rejects, as well as mineral matter in the coal itself which is available in the fly and bottom ash when the coal is burned (9). Of the Canadian sources of high aluminum-bearing coal wastes, the deposit which appears to have the greatest potential is at Hat Creek, B.C. This deposit is in the early stages of development for thermal power generation. The magnitude of the deposit - in excess of 10^9 t - and the high alumina content of the ash - 27 to 33% Al_2O_3 - warranted investigation of this material (10,11,12,13).

Two cubic metres of Hat Creek material classified as coaly waste from Trench A were obtained from B.C. Hydro and Power Authority. The material was sized, blended and burned by CANMET's Canadian Combustion Research Laboratory (CCRL) in its pilot-scale, 25-cm diameter atmospheric fluidized-bed unit. The analysis of the material is given in Table 3.

The temperature range normally used in fluidized-bed combustion of coal is similar to that required to dehydroxylate clay. As the inert

Table 3 - Analyses of Hat Creek coaly waste

Proximate (air dried)	%	Ultimate (air dried)	%	Ash analysis	%
Moisture	18.10	Carbon	23.36	SiO_2	59.45
Ash	44.67	Hydrogen	2.09	Al_2O_3	30.82
Volatile matter	22.41	Sulphur	0.45	Fe_2O_3	5.50
Fixed carbon (by diff)	14.74	Nitrogen	0.95	TiO_2	1.06
		Ash	44.67	P_2O_5	0.01
		Oxygen (by diff)	10.30	CaO	0.96
				MgO	1.16
				SO_3	1.39
				Na_2O	0.17
				K_2O	0.76

material in the waste coal is primarily kaolin, an investigation was made to determine whether alumina could be recovered from fluidized-bed ash. About 25 combustion test runs were made by CCRL covering the temperature range of 700 to 1050°C in 50°C intervals. Both the bed ash and the cyclone ash were collected; the mass ratio of bed: cyclone ash being approximately 2:1. The particle size of the bed ash was 80% minus 3.36 mm, plus 210 um, and of the cyclone ash 80% minus 150 um. In most cases the bed ash was pulverized to minus 850 um for leaching.

ACID EXTRACTION OF ALUMINUM FROM FLUIDIZED-BED ASH

Ash samples from the combustion of waste coal over the temperature range of 700 to 1050°C were leached in 26 m % hydrochloric acid at the reflux boiling temperature of 108°C. the resultant extraction of aluminum versus fluidized-bed temperature is shown in Fig. 5. Optimum aluminum solubility of 80 to 85% is obtained from ash in the 750 to 850°C range. This is the range normally used to dehydroxylate clay. There was a severe decrease in extraction of alumina from ash resulting from combustion at the higher temperature range of 850 to 900°C, particularly with bed ash. In that range both the actual temperature and duration of time the material was exposed to it have a critical effect on aluminum solubility as it is also in this range that insoluble aluminosilicates

start to form and crystallize. Thus, the extraction from cyclone ash was higher than bed ash because the fine particles were rapidly elutriated from the combustion zone by the fluidizing air.

The majority of experimental work was conducted on ash combusted at 800°C. An exothermic reaction rapidly brought the leach slurry to reflux boiling temperature when ash was added to 90°C acid. Between 65 and 70% of the total aluminum was extracted within the first 5 min of leaching. Extraction in the order of 80% was achieved
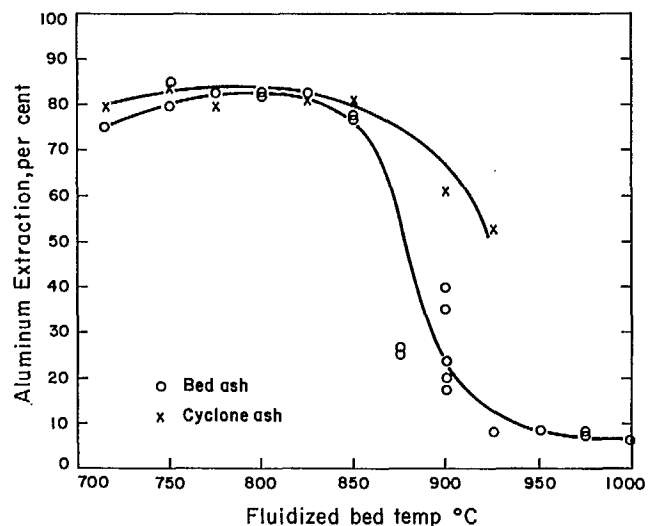

Fig. 5 - Effect of fluidized-bed temperature on aluminum extraction from -850 um bed ash and from cyclone ash in a 2 h, 26 m % HCl leach at 108°C

within 30 min. Thereafter, it increased very slowly to about 85% in 4 h. As expected, the optimum extraction occurred at or near the reflux boiling temperature of the acid. The activation energy was determined from the initial rate data for 800°C ash in either 26 m % HCl or 50 m % H_2SO_4 as 15 kcal mole^{-1}. Leach tests of various screen fractions indicated that no additional extraction occurred when material was crushed finer than 850 µm. Material coarser than this exhibited lower extractions for the same leach duration.

FLUOSILICIC ACID-ASSISTED LEACHING

As previously discussed, aluminum extraction from bed ash decreased dramatically above 850°C. The normal temperature range for fluidized-bed technology burning coal is 800 to 900°C. Whereas it would be feasible to control the temperature below 850°C when burning waste coal for alumina feed, the ash from coal burned for power generation with fluidized bed technology could be the less soluble material. In an attempt to extend the temperature range of ash from which aluminum could be extracted, experiments were made with additions of fluosilicic acid to the leach liquors.

Varying amounts of fluosilicic acid were added to the leaches. It was found that a relatively large amount of acid was necessary to be effective, the maximum being 0.225 mol H_2SiF_6/mol Al_2O_3 in the feed. It was also found that the leach duration had to be increased to about 4 h. Under these conditions aluminum extraction from 850 to 900°C ash was in the 80% range. Figure 6 compares aluminum extraction obtained from 875° and 900°C ash with and without fluosilicic acid addition.

HYDROFLUORIC ACID-ASSISTED LEACHING OF FLY ASH

While on the subject of fluoride-assisted leaching, some preliminary experimentation was done by L.G. Ripley on acid extraction of aluminum from conventional thermal power combustion fly ash (14). This material had been subjected to high temperatures during combustion and is poorly reactive in the usual mineral acids. Three fly ashes were examined: Hat Creek, 28.63% Al_2O_3; White-
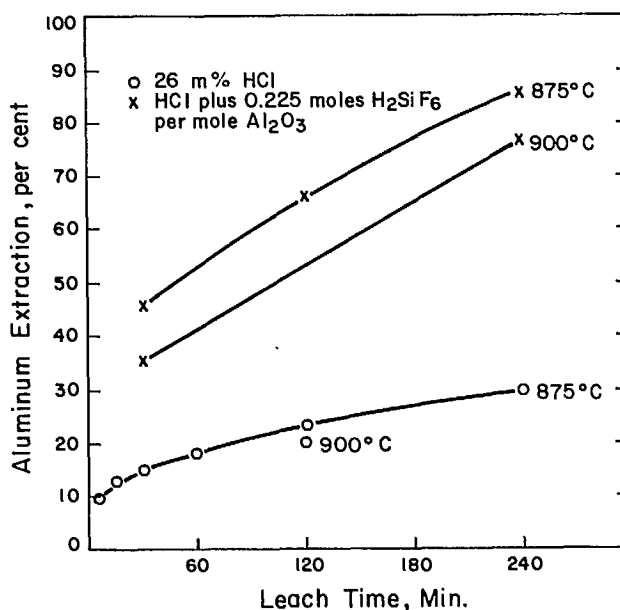
Fig. 6 – Effect of leach duration and H_2SiF_6 on aluminum extraction from ash in 26 m % HCl at 108°C, -0.841 µm ash

wood, 23.07% Al_2O_3; and Sundance, 23.27% Al_2O_3. Tests were carried out by varying the addition of hydrofluoric acid, the maximum amount being in the proportion of 0.086 HF:1.0 HCl. Experiments with hydrofluoric acid were done in a closed Teflon-lined bomb, usually at 100°C and usually for 4 h. Aluminum extraction was not particularly high, the maximum being about 70% for Hat Creek ash. Extractions could possibly have been improved with a greater HF content. Some results are presented in Table 4.

Table 4 – Extraction of aluminum from
-75 um fly ash in a 4-h leach
with 20 m % HCl at 100°C

Fly ash	HCl:HF	
	0	1.0:0.086
Whitewood	29.1%	35.5%
Sundance	43.3	57.9
Hat Creek	47.1	71.7

RECOVERY OF ALUMINA

The first part of this report reviewed the acid extraction of aluminum from anorthosite, clays and coal wastes. Extraction tests were conducted principally with hydrochloric acid, to a lesser extent with sulphuric acid and occasionally with nitric acid. Numerous processes have been devised to recover alumina from these acids, some of which were reviewed in reference 15.

The majority of the alumina recovery work was done using the hydrochloric acid-gas sparge process. The sulphuric acid leach-hydrochloric acid gas sparge process was tried in some early tests. The most advanced sulphuric acid process, that is, the H Plus Process, was not studied in detail as it is a proprietory process of Alcan International and Aluminum Pechiney. A hydrochloric acid-caustic purification technique was developed for use on fluidized-bed ash. For this project it was necessary to develop the analytical capability for measuring impurities at very low concentrations. Consequently, the alumina products in the early tests were analyzed only semi-quantitatively.

Similar processes were used to recover alumina from anorthosite, clay and coal ash. As the work on fluidized-bed ash was perhaps the most advanced, subsequent data will be principally on that material. Regardless of whether the feed material was anorthosite, clay or fluidized-bed ash, the acid leach dissolved not only aluminum but also any soluble impurity. The principal impurities were: Fe, Ca, Mg, K and Na, and the minor impurities were V, Ti, Zn, Ni, P, Cu, etc. Although the quantities varied with the feed material, all were present to some extent. The solubilization of these impurities consumes acid which must be recovered. More important, however, is incorporation of the impurities in alumina.

HYDROCHLORIC ACID-GAS SPARGE PROCESS

In this process the aluminum-bearing material is attacked with hydrochloric acid, the soluble aluminum and impurities are separated from the siliceous residue and the aluminum is recovered from the leachate by sparging with hydrochloric acid gas to crystallize aluminum trichloride hexahydrate. The salt is dissolved in dilute acid or water and recrystallized to purify it prior to calcining to alumina. A conceptual flowsheet for the process is given in Fig. 7.

The material preparation and leach extraction results have already been discussed. Those tests used fresh acid; however in actual practice the filtrate from the first crystallization step, which is 26 to 30 m % HCl as a result of sparging, would be recycled back to the leach stage. Unless a portion of this stream is bled off, the impurities in the leachate increase dramatically. Figure 8 shows the impurity buildup over 10 leach cycles of fluidized-bed ash with 8% bleed.

SOLID-LIQUID SEPARATION AND EVAPORATION

Following leaching, the pregnant liquor was separated from the siliceous residue by vacuum filtration. With clay or fluidized-bed ash, filtration and cake washing were rapid. Anorthosite filtration was much slower due to the finer particle size. The use of fluosilicic acid in anorthosite leaching tended to cause the residue to cake on the filter, thus making subsequent washing more difficult and necessitating a repulp step.

In the case of fluidized-bed ash, the leach liquor, diluted by wash water in the solid-liquid separation, was reconcentrated prior to crystallization. By evaporating a volume equal to the volume of wash water added the resultant liquor had an aluminum concentration of 60 to 65 g/L Al. The more concentrated is the pregnant liquor, the less hydrochloric acid gas is required for sparging.

SOLVENT EXTRACTION

One of the major impurities in clays or ash is iron which dissolves during the leach as ferric chloride. The ferric ion can be removed from the leachate by solvent extraction with ethyl or isopropyl ether, with cyclohexanone or with amine. Some experimental work was done using a ratio of Alamine 336:isodecanol:kerosene in 10:10:80. There was no difficulty in removing

Fig. 7 – Flowsheet of HCl process for fluidized-bed ash

iron from the leach liquor using an organic:aqueous ratio of 1.0:1.0 or greater. The alumina from a single crystallization stage after solvent extraction met the iron specification. Unfortunately, the extractants evaluated for solvent extraction had little effect on removing the other impurities e.g., P, Mg, and Cr. Removal of these impurities required double crystallization of aluminum trichloride hexahydrate. The double crystallization technique lowered the iron content, regardless of whether solvent extraction had been used, to within specification so there was essentially no particular advantage to using solvent extraction.
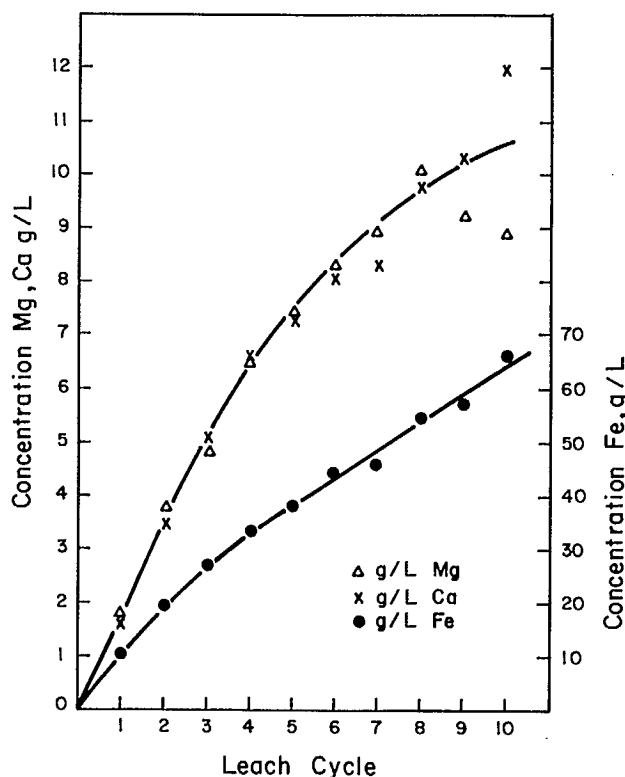
Fig. 8 - Impurity concentration in leachates

CRYSTALLIZATION

The crystallization of aluminum trichloride hexahydrate, $AlCl_2 \cdot 6H_2O$, is based on the decreasing solubility of the salt with increasing hydrochloric acid concentration. This was accomplished by sparging the leachate with HCl gas. Heat is evolved during the absorption of HCl gas in the liquor, consequently a water bath was required to maintain the desired temperature. The crystallization of $AlCl_3 \cdot 6H_2O$ was not particularly temperature sensitive; however, the incorporation of impurities either by absorption onto the aluminum salt or precipitation as solid chlorides, e.g., NaCl, $MgCl_2 \cdot 6H_2O$, was found to be temperature sensitive. The crystallization of some impurities, especially Fe, was also dependent on the concentration of hydrochloric acid to which the liquor was sparged. Generally the higher hydrochloric acid content, e.g., 32 m % HCl, resulted in a higher impurity content in the crystallized aluminum salt.

With any of the Canadian non-bauxite alumina sources as feed material, the aluminum salt from a single crystallization contained an excess of many impurities as shown in Table 5. In the case of anorthosite the major impurity was NaCl which amounted to several per cent. To purify the $AlCl_3 \cdot 6H_2O$ it was filtered, washed with concentrated acid, redissolved in water and crystallized a second time by sparging. The temperature of the first crystallization stage was normally maintained at 40°C and the second stage at 60°C. Vacuum filtering and acid washing of the salt also followed the second stage crystallization.

CALCINATION

The $AlCl_3 \cdot 6H_2O$ salt is decomposed by heat to Al_2O_3, HCl and H_2O. The decomposition starts at 118°C but complete conversion requires calcining to about 1000°C. Some experimental work was done using a fluidized-bed unit to calcine the aluminum salt to alumina at 400°C. This material was water leached to remove the unreacted chlorides of Ca, Na, Mg and K. The washed alumina was calcined to 1100°C.

ACID RECOVERY

Preliminary experimental work was conducted to recover acid from contaminated bleed liquor. One approach was to react the bleed liquor with strong sulphuric acid; with this technique Ca, Mg, Fe, etc. chlorides were converted to sulphates thus releasing hydrochloric acid gas. HCl recovery was not determined. Another approach tried was the thermal decomposition of waste chlorides in a fluidized bed. The bed material was siliceous residue from leaching and the temperature was 600 to 800°C. Steam was required to completely decompose $CaCl_2$ with this method. Better than 90% recovery of HCl was achieved.

ALUMINA PURITY

The principal objective of this work was to develop processes capable of producing cell-grade alumina from non-bauxite sources. The target specifications for cell-grade alumina are quite stringent and are given in Table 5. Also in the table are the average concentrations of

Table 5 - Alumina by the hydrochloric acid-gas sparge process average of 10
leach cycles, ug/g

Element	Target	1st crystallization	2nd crystallization	Water leached calcine
Fe	200	>1000	42	24
Si	115	84	52	60
Mg	12	>1000	102	14
Ca	600	430	37	na
Cr	12	121	35	22
V	11	107	6	na
Na	3000	>1000	>1000	na
Mn	12	18	>8	na
Zn	160	27	>25	na
Ti	30	37	5	na
P	4	na	na	35*
K	40	52**	na	>6**

na - Not analyzed

* - average 5 samples

** - one sample

impurities in alumina produced from 10 leach cycles of fluidized-bed ash. The impurities - Mg, Cr, and P - could not meet the target specification with double crystallization. Low temperature calcination to 400°C followed by a water leach reduced Mg and Cr close to specifications, but the individual cycle results were erratic. Phosphorus was always 5 to 10 times the 4 ug/g concentration.

HYDROCHLORIC ACID LEACH-CAUSTIC PURIFICATION PROCESS

Because of the difficulties in producing pure alumina from fluidized-bed ash by the hydrochloric acid-gas sparge process, an alternative hydrochloric acid leach-caustic purification process was tried. In this, a hydrochloric acid leach was used to extract the aluminum and the soluble impurities from the siliceous residue. After separation from the silica, the leachate was evaporated to dryness and calcined to 400°C to produce a crude alumina. The crude alumina was water leached to remove soluble chlorides and then used as feed material for a modified Bayer pro-

cess. It was pressure digested with sodium hydroxide to produce sodium aluminate liquor and a red mud residue containing the impurities. After separation from the red mud, the sodium aluminate liquor was seeded to precipitate alumina trihydrate which was calcined to alumina. A conceptual flowsheet is given in Fig. 9. The alumina product should have essentially the same composition and characteristics as alumina produced from bauxite with the Bayer process.

ALUMINUM EXTRACTION

The raw material was the same as for the previously described process. The leaching stage was also similar in acid concentration, temperature and time; however there was no recycling of contaminated acid. Following leaching, the pregnant liquor was separated from the siliceous residue. A minimum of wash water was used as all water must subsequently be removed by evaporation.

EVAPORATION AND CALCINATION

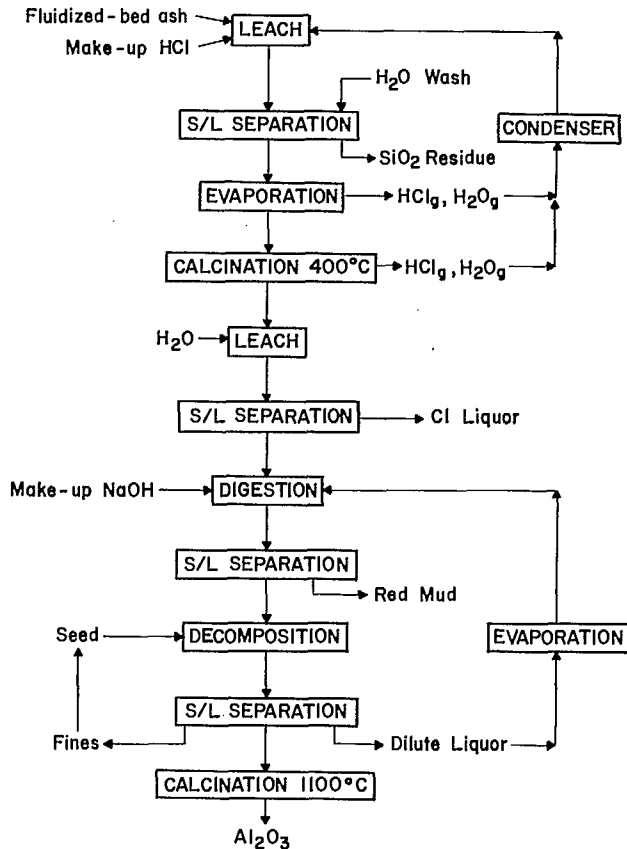The aluminum-bearing liquor was evaporated to dryness and calcined. Satisfactory calcines

Fig. 9 — Flowsheet of hydrochloric acid—caustic purification process

were obtained in a minimum of 3 h at 350°C in a small fluidized bed. Larger amounts of calcine, up to several hundred grams, produced in a muffle furnace required 400°C. A good calcine was tan brown indicating conversion of ferric chloride to oxide. Under these conditions magnesium chloride partially decomposed to oxides and oxychloride, but calcium, sodium and potassium were not significantly decomposed.

POST CALCINE LEACH

The crude alumina produced by calcination was typically 83% Al_2O_3 and contained 5 to 7.5% Cl, presumably as alkali and alkaline earth chlorides. The material was very hydroscopic. A water leach at 60°C effectively removed most of the chloride salts. Analyses of a calcine and leached calcine are given in Table 6. The alumina

was very reacive and hydrolysed to boehmite, $Al_2O_3 \cdot H_2O$, during the water leach.

CAUSTIC PURIFICATION

The washed and dried crude alumina was digested with 215 g/L NaOH at 200°C in an autoclave for one hour. Calcium hydroxide was added to precipitate phosphorus. Under these conditions 92 to 95% of the aluminum in the feed was recovered as sodium aluminate liquor. The impurities, principally iron, were precipitated as red mud residue. The digestion conditions were not optimized. The liquor, including wash, typically analyzed 108 to 130 g/L Al_2O_3 and 95 to 130 g/L Na_2O.

The sodium aluminate liquor was decomposed to alumina trihydrate by maintaining the liquor at 50°C for 75 h. Fine alumina trihydrate seed was added to nucleate the precipitation. Typically 50% of the aluminum content in the liquor was converted to alumina trihydrate, $Al_2O_3 \cdot 3H_2O$. The trihydrate was calcined to alumina to 1100°C. The now depleted liquor was concentrated by evaporation and recycled to the caustic digestion stage.

The objective of this work was to produce an alumina product meeting cell-grade specifications. Table 7 gives the purity of alumina produced over three digestion and decomposition cycles. All impurities are within specification.

Table 6 — Analyses of calcines

	Calcine 3 1/2 h 400°C	Washed calcine dried 105°C
	m %	m %
Al_2O_3	83.6	70.2
Fe_2O_3	14.1	11.9
CaO	2.67	0.05
MgO	1.43	1.16
P_2O_5	na	0.184
Na_2O	na	<0.01
K_2O	na	<0.01
Cl	7.55	0.14
LOI	na	20.26

Table 7 - Alumina by the hydrochloric acid-
caustic purification process,
average of 3 cycles, ug/g

Element	Target	Analyses
Fe	200	60
Si	115	<40
Mg	12	<8
Ca	600	47
Cr	12	<6
V	11	<5
Na	3000	1500
Mn	12	<8
Zn	160	70
Ti	30	<5
P	4	<4

CONCLUSIONS

The emphasis of the CANMET work on acid processes for the extraction and recovery of alumina from Canadian non-bauxite sources was on hydrochloric acid techniques as they and the H Plus process are considered the most advanced technologies for alumina recovery. Although the work was on a laboratory scale, it did show that aluminum could be extracted from domestic anorthosite, clays and fluidized-bed ash and that alumina of cell-grade quality could be recovered.. Preliminary costing indicated that all processes are slightly more expensive in both capital and operating costs than the Bayer process using bauxite. Should the need arise to produce alumina from non-bauxite sources in Canada the data produced by this project may provide a foundation upon which to build.

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