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ALUMINUM EXTRACTION FROM FELDSPAR

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TRADITIONAL ORE

Any industrial effort in space will need aluminum, but the usual ore on Earth is bauxite. That mineral is formed by tropical rain forests; igneous minerals are weathered by water into hydrated minerals such as clay, then the tropical ecosystem depletes elements they need leaving iron oxide, silicon dioxide, and aluminum oxide. Those three oxides together are bauxite. Technically bauxite is a stone and the exact mineral form of each oxide varies from deposit to deposit. We aren't going to find a tropical rain forest on the Moon or Mars, so we have to get aluminum from an igneous mineral.

MARS MINERALS

What do we have? Feldspar is plentiful on celestial bodies and contains a lot of aluminum. One sample from the Moon returned by Apollo was pure anorthite. The Thermal Emission Spectrometer on Mars Global Surveyor detected a lot of feldspar including microcline, andesine, and a lot of bytownite.

Plagioclase feldspar is a group. Anorthite has an aluminum:silicon ratio of 1:1 while Albite has a ratio of 1:3. Microcline is considered orthoclase feldspar; it's similar to albite, the only difference is sodium replaced by potassium.

Feldspar with an aluminium:silicon ratio of 1:1 will dissolve in hydrochloric acid. Other forms of feldspar such as albite or microcline will be etched but not dissolve because they have an aluminium:silicon ratio of 1:3. That works because the 1:1 ratio leaves silicon oxide tetrahedra isolated, so it dissolves as silicon dioxide. A 1:3 ratio results in direct Si-O-Si bonds that do not break. Basically, hydrochloric acid dissolves the surface layer of grains of albite or microcline but silicon oxide accumulates as a layer of quartz. Quartz does not dissolve so once the layer is built, dissolution stops. The good news is anorthite and bytownite do dissolve.

TRADITIONAL SMELTING

The traditional process to extract aluminum from ore involves two major processes. The Bayer process extracts alumina from bauxite via a chemical process and is usually done at the mine site. Pure alumina is exported to a smelting operation. The Hall-Héroult process uses electricity to de-oxidize alumina into aluminum metal. It's usually done near a major electric power source.

BAYER PROCESS

The Bayer process dissolves alumina and silica from bauxite ore using sodium hydroxide, also known as caustic soda. Iron oxide, titanium oxide, and other materials don't dissolve. This waste is red in colour so is usually referred to as red mud. The solution is drawn off and CO_2 is blown in under pressure. This dissolves to form carbonic acid which neutralizes the alkali causing aluminum hydroxide to precipitate. When pressure is released, CO_2 gas bubbles off like soda pop. Aluminum hydroxide is collected and rinsed so the sodium hydroxide can be recycled. Aluminum hydroxide is calcinated, which means it's baked hotter than boiling temperature of water but less than melting. This causes oxygen from the air to combine with hydrogen from aluminum hydroxide to form alumina and water vapour. Aluminum hydroxide calcinates above 230°C.

HALL-HÉROULT PROCESS

Since alumina is an electrical insulator, the hall process uses cryolite (Na_3AlF_6) as a catalyst for electrolysis. Molten cryolite dissociates into an ionic compound permitting electrical conduction. Alumina breaks down into liquid aluminum, which sinks to the bottom of the vat, and oxygen bubbles off. Molten aluminum is poured from a spout at the bottom.

Side reactions are a concern. Electricity is delivered to the molten cryolite via a carbon anode. Much of the oxygen released by electrolysis will combine with carbon from the anode to form carbon dioxide and carbon monoxide gasses. This consumes the anode. Carbon can be regenerated from carbon dioxide via the Reverse Water Gas Shift. Most Mars Society members will be familiar with this, but perhaps not aware that with enough heat and pressure the process will continue to consume carbon monoxide to form carbon soot. Soot can be poured into a mould and baked under pressure to reform graphite; the process takes about 3 days. Söderberg anodes deliver a paste of coke dust and pitch to continuously reform anodes, but that requires pitch.

One potential area of research is to continuously form reform graphite anodes using the heat of electrolysis. This is another spin-off for terrestrial application. Recycling CO_2 and CO into anodes and O_2 would eliminate the need for coke and pitch, and produce oxygen that can be sold as a byproduct. Although the reverse fuel cell to recover hydrogen would consume more electricity, this would have a net reduction of operating cost.

BYTOWNITE TO ALUMINA

Bytownite is an alkali feldspar so an alkali like sodium hydroxide will not dissolve it. Hydrochloric acid will. The solution of aqueous hydrochloric acid with have ions with nominal molar proportions of 1.8 Al^{3+}, 0.8 Ca^{2+}, 0.2 Na^{+}, and aqueous 2.2 SiO_2. It may have a small proportion of K^{+} from microcline. Dissolution rate increases with temperature and strength of acid, ideal pH 1.0 @ +200°C. This is above boiling so it would require a pressure cooker.

Ammonia is an alkali when dissolved. Just as carbon dioxide is used to neutralize pH of sodium hydroxide in the Bayer process, ammonia will neutralize pH of sulphuric acid. Aluminum hydroxide with precipitate once pH is neutral, specifically between 4.5 and 9.2. Ammonium chloride has pH 5.5 (1% aq. sol), 5.1 (3% aq. sol.), 5.0 (10% aq. sol.)

Then aluminum hydroxide can be calcinated into alumina just as with the Bayer process.

Sodium chloride is normal table salt. Calcium chloride and potassium chloride are also salts, they will remain in solution when pH is neutralized.

Silica scale is a problem with the Bayer process, normally controlled by selecting bauxite with little silica to start with. Bytownite will have more silica, so this is a concern.

SIDE REACTIONS: AMMONIUM CHLORIDE

Ammonia will form an alkali in water: $NH_3 + H_2O$ _ $NH_4^+(aq) + OH^-(aq)$.
Ammonia (NH_3) will bind with hydrochloric acid to form ammonium chloride, sal ammoniac (NH_4Cl). Ammonia boils at -33.5°C. Ammonium chloride melts at +338°C, boils at +520°C, dissolves in water; pH 5.5 (1% aq. sol), 5.1 (3% aq. sol.), 5.0 (10% aq. sol.). This demonstrates that ammonium chloride will form during gas precipitation of ammonia, but it can be removed and washed back into the reaction vessel with a water shower scrubber.

ACID RECYCLING

Producing hydrochloric acid from brine is one of the best documented chemical processes. Electricity across a membrane will separate sodium chloride, depleting salt on the anode side while concentrating sodium hydroxide on the cathode side. Chlorine gas is evolved at the anode, hydrogen gas at the cathode. Hydrogen will burn in chlorine to produce hydrogen chloride. When dissolved in water that's hydrochloric acid. There are other methods that produce hydrochloric acid directly, but they involve other chemicals such as sulphur dioxide.

Potassium is just two elements up the periodic table from chlorine, and calcium is next; so a membrane impermeable to chlorine won't let potassium or calcium cross. This means depleted brine will contain all the potassium and calcium salt. Caustic soda on the cathode side will be pure sodium hydroxide.

Chlorine can be recovered from potassium and calcium by electrolysis in a diaphragm cell. A diaphragm cell isn't as energy efficient as a membrane cell, but it will still produce hydrogen and chlorine gas. The product will be primarily calcium hydroxide with a little potassium hydroxide.

PRECIPITATING SILICA

There is some debate whether silicon exists as aqueous silicon dioxide or silicon hydroxyl. The paper on anorthite dissolution by Eric H. Oelkers and Jacques Schott indicates that dissolution in hydrochloric acid will result in aqueous silicon dioxide, however work by a couple groups studying geothermal plants found silicon hydroxyl. Perhaps it depends upon mechanism of dissolution. In any case, one geothermal group precipitated mesoporous silica using alumina beads while the other polymerized silica hydroxyl to precipitate colloidal silica aggregates then calcinated them to form silica.

It's interesting that both use hydrochloric acid and sodium hydroxide to control pH, the same chemicals we need to dissolve bytownite ore. It appears silica will spontaneously precipitate in a high salt concentration. Increased salt causes rapid precipitation and large colloids, which will agglomerate unless a dispersant is added.

Amorphous silica is glass, so it's quite useful. Soda-lime glass requires the addition of sodium carbonate, or sodium hydroxide and calcium carbonate. Calcium carbonate could be in the form of calcite $Ca(CO_3)$ and/or dolomite $CaMg(CO_3)_2$. Sodium carbonate would have to be manufactured; but calcite and dolomite exist in Mars soil, although the concentration is debated. The proton mode of the APXS instrument on Sojourner didn't work, and it was known not to work before launch of the Mars Exploration Rovers Spirit and Opportunity, so we have no direct measurement of carbon content in Mars soil.

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TABLES

Surface type 1	Model-derived modes (%)
Microcline1	5.8
Andesine	22
Bytownite	21.5
Bronzite	5.4
Augite1	12.4
Augite3	11.3
Serpentine	4.8
Gypsum	1.8
Calcite	3.7
Dolomite	0.9
Kaolinite	2.4
Illite	9.9
	RMS error (emissivity) = 0.179

Surface type 2	Model derived modes (%)
Microcline1	5.7
Bytownite	27
Actinolite	6.1
Muscovite	5.7
Bronzite	1.6
Augite1	8.4
Forsterite	2.9
Gypsum	4.5
Dolomite	3.3
Fe-smectite	9.2
Illite	2.2
Obsidian Glass	22.8
	RMS error (emissivity)= 0.089

Table 1: Deconvolution results for Martian surface spectral types 1 and 2.
Source: A Global View of Martian Surface Compositions from MGS-TES, Joshua L. Bandfield, Victoria E. Hamilton, Philip R. Christensen, Science Vol. 287, 3 March 2000

Plagioclase feldspar

Anorthite	$CaAl_2Si_2O_8$
Bytownite	70-90% anorthite, 10-30% albite
Labradorite	50-70% anorthite, 30-50% albite
Andesine	30-50% anorthite, 50-70% albite
Oligoclase	10-30% anorthite, 70-90% albite
Albite	$NaAlSi_3O_8$

Orthoclase feldspar

Microcline	$KAlSi_3O_8$

Table 2: Forms of feldspar.

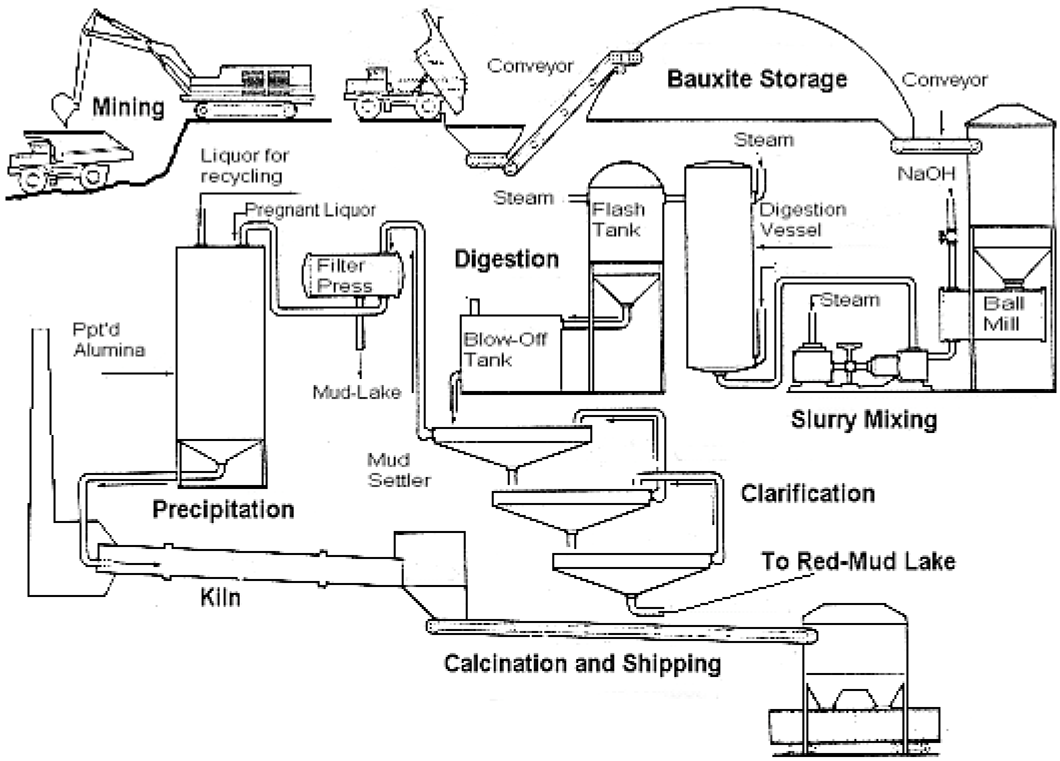

Figure 1: Typical bauxite mine operation.

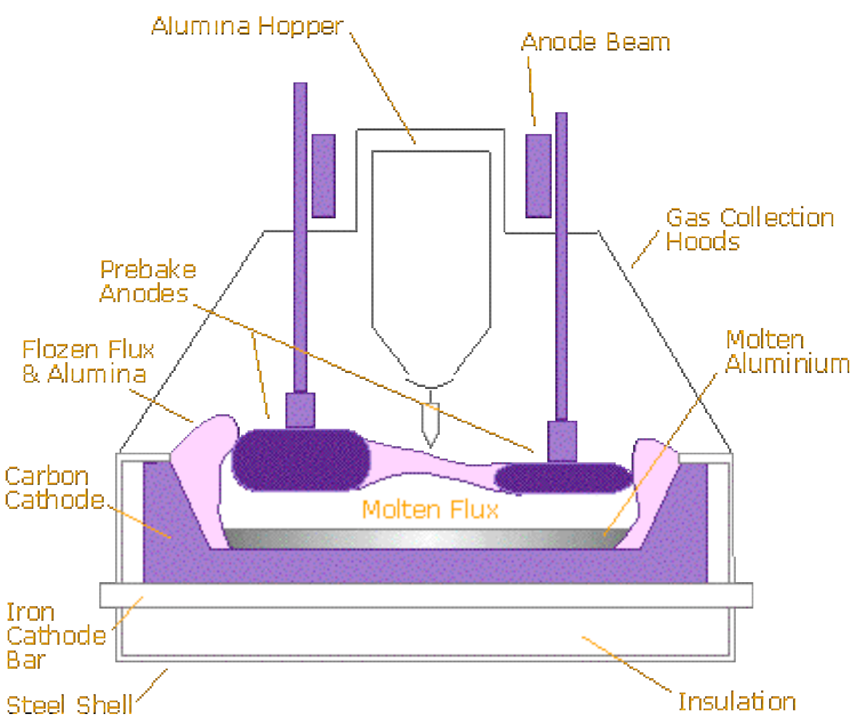

Figure 2: Hall-Héroult electrolysis cell, with replaceable anodes.

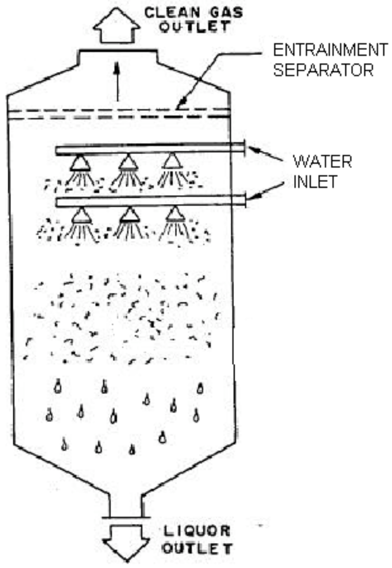

Figure 3: Shower scrubber to remove ammonium chloride.

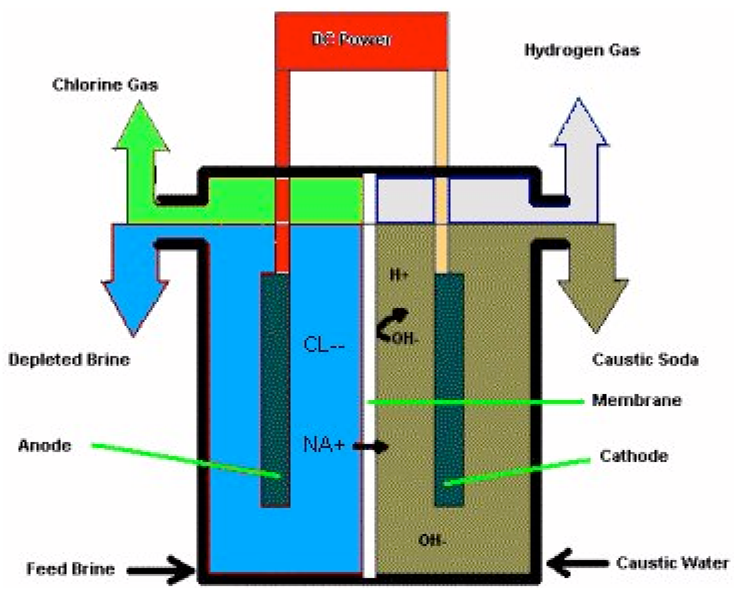

Figure 4: Membrane electrolysis cell to recycle acid. Feed brine with sodium chloride salt is fed in one side, depleted brine with potassium chloride and calcium chloride salts is passed on to a diaphragm cell. Water fed in the other side is returned with caustic soda (sodium hydroxide). Hydrogen and chlorine gasses are burned together to form hydrogen chloride; when dissolved in water that is hydrochloric acid.