Abstract.

Six samples of commercially traded waste aluminium of differing types were processed using the NetZeroChem proprietary system to determine their suitability for use to generate useful quantities of clean hydrogen gas together with aluminium hydroxide / aluminium oxide of commercially tradeable quality. Although the process chemistry produces abundant heat, of the order of 4MWth per tonne, this was not measured on this occasion since the heat output has been determined both theoretically and practically in previous tests, and is well reported in the literature.

A controlled temperature argon-purged reactor system was employed in order to better determine gas evolution rates, gas purity was measured using a capillary gas feed into a Hiden Hal 100 gas analysis spectrometer and gas flow-rates and total yield/vs time using a Sierra hydrogen flowmeter and data collection system. A control comparison test was performed using 99.7% pure Al granules >1mm (APC Chemicals UK CAS7429-90-5). Optical microscopy and LOI testing etc. was performed on the hydroxide samples produced, but due to the current pandemic emergency we were unable to perform deep analysis or electron microscopy, so have included some information from earlier tests on comparable materials.

Background.

There are several advantages to using lower value and hard to re-smelt aluminum as a primary source of hydrogen energy. The principal by-product, $Al(OH)_3$, may be used to synthesize other chemical feedstocks while hydroxide and the derived oxide are valuable and have many uses, for example ranging from insulators to refractories and pharmaceuticals, also the recovery of aluminum from its hydroxide is possible. The hydrogen generated by the process is pure; therefore, it can be used in devices that require high purity like fuel cells. Finally, because the catalyst mix employed is not consumed in the reaction it can be recovered and reused.
Six different aluminum tri-hydroxides $Al(OH)_3$ are known, the differences are those of molecular structure; Gibbsite, Bayerite, and Nordstrandite. Two monohydroxides; (AlOOH) Boehmite and Diaspore, also a final very dehydrated type, Tohdite ($5Al_2O_3,H_2O$). Gibbsite, Bayerite, Diaspore and Boehmite are found in bauxite clays, but all these aluminates can be produced by various thermal or precipitation processes in the laboratory or on industrial scale.

Commercial and Environmental Matters (in brief)

The process we have developed is able to utilise many of the diverse streams of aluminium scrap that are concentrated at recyclers and waste transfer/sorting depots. These include cans, turning and drilling waste, chopped wire and so on. Small particle sizes are best for this process, and these are the types of waste least suited to re-smelting requiring above the norm energy input and creating more polluting dross, thus they achieve the lowest market values.

Using these materials to make hydrogen and aluminium compounds instead of re-smelting them is actually advantageous in environmental terms, since while bauxite clay mining – the primary source of aluminium hydroxide - uses less than 1.5 kilograms of diesel (mostly for haulage) and around 5 kWh of electricity per tonne, the next step is energy intensive. The Bayer Process which transforms bauxite into alumina for electro-smelting into metal consumes around 14.5 GJ (400kWh) per tonne of alumina, of which around 150 kWh is electrical input and the rest is transport and process chemicals. Every tonne of alumina so produced creates 1 tonne of CO_2.
Around 92-95% of global alumina production is smelted into metal, but the balance is sold directly to industry as it is a valuable and versatile raw material with countless uses..

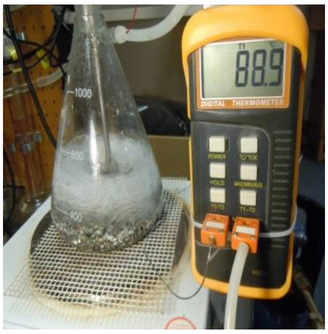
It is easy to see that creating fresh alumina and abundant energy from low value raw materials close to places where they are found and supplying that alumina to local industry directly the huge amount of energy used for mining, refining, and transporting bauxite is eliminated. Since the process is zero CO2 and also energy positive the savings look like this.

To make 1 tonne of refined and calcined alumina (aluminium oxide) from bauxite clay consumes a total of 4.1MW. This includes the energy required to mine and move the clay, and the chemicals and electrical energy used in the Bayer Process but excludes the energy cost of shipping from S.America, the Persian Gulf, China, or Australia – the main producers.

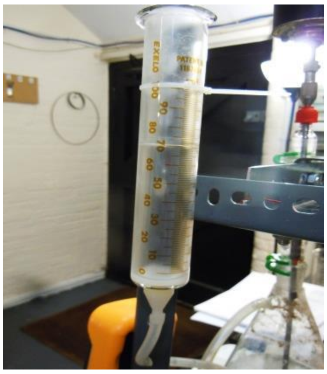
To make one tonne of calcined alumina using the NetZeroChem process requires 0.5 tonnes of aluminium scrap. This produces 4 MW – that is 2,000 kWh of hydrogen energy and 2,000kWh of process heat, though the calcining stage used to transform the aluminium hydroxide produced as the first product into alumina reduces the overall figure from 4MW to 3.5MW. As production uses local raw materials and is for local users transport costs are low and the total positive energy of the process over mined production is 3.5 + 4.1 = 7.6 MW/tonne energy gained and saved and 1 tonne less of CO2 produced. A further bonus is that this process obviates the dumping of 2 tons of mine waste.

Source:- http://bauxite.world-aluminium.org/refining/energy-efficiency/

Methodology. Gas Purity/Volume Tests.

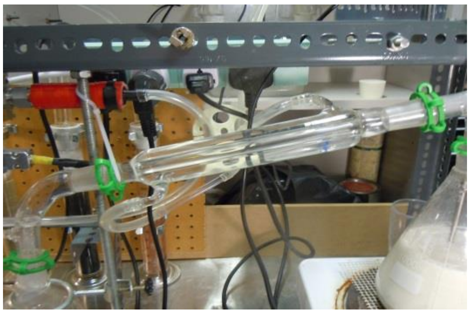


The analytical reactor system consists of a 1 litre borosilicate flask on a thermostatic hotplate. Water and gas temperatures are monitored using a 2 channel K-type thermocouple meter. The reactor contents are stirred throughout each experimental run. The 50 gram aluminium sample and 450 ml of de-gassed (by pre-boiling) de-ionised water are placed in the reactor vessel and the gas cooling and scrubbing section is then fitted into it.

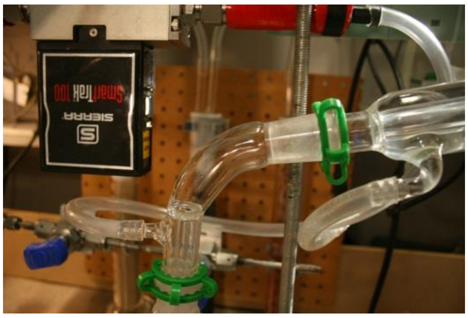


Catalyst mix is added using a 100ml syringe, system temperature is carefully monitored to keep it within the range 80-90C. This is to prevent the water from boiling which would flood the system with steam. The reactor contents are stirred continuously throughout the whole process

As soon as the catalyst is added a vigorous reaction begins. Hydrogen bubbles rise to the surface and are fed to the gas cooling system. The reactor contents become milky white due to the suspended aluminum hydroxide created by the reaction between aluminium scraps and water.

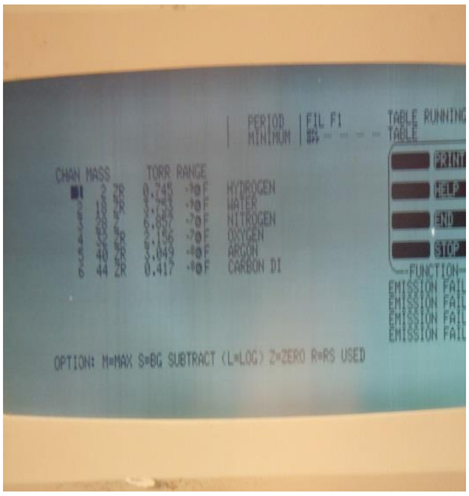


The hydrogen passes through a standard Leibig condenser with pumped cold water circulation. Water vapour present in the hot gas is condensed into a flask at the bottom left of the picture.



The Sierra flow-meter on the left of the picture is a highly accurate instrument especially calibrated to measure hydrogen gas. Data is passed from the Sierra to a LabJack data system and stored in a dedicated programme on a portable computer.

This 'under test and construction' shot shows the next stage, here the gas is scrubbed clean of any residual impurities be passing through the three tall cylinders at the back of the shot. The first is filled with slightly acidified water, the second with activated carbon, and the third with zeolite drying grains to remove remaining traces of water vapour.



The final stage of the gas analysis uses a gas Quad Mass spectrometer. This gas analyser is capable of detecting and measuring all significant impurities down to 'parts in a billion' level and has been specially programmed to detect those impurities of particular concern to fuel cell operators, these include Carbon Monoxide, Sulphur Dioxide

Samples Tested , Procedures and Results

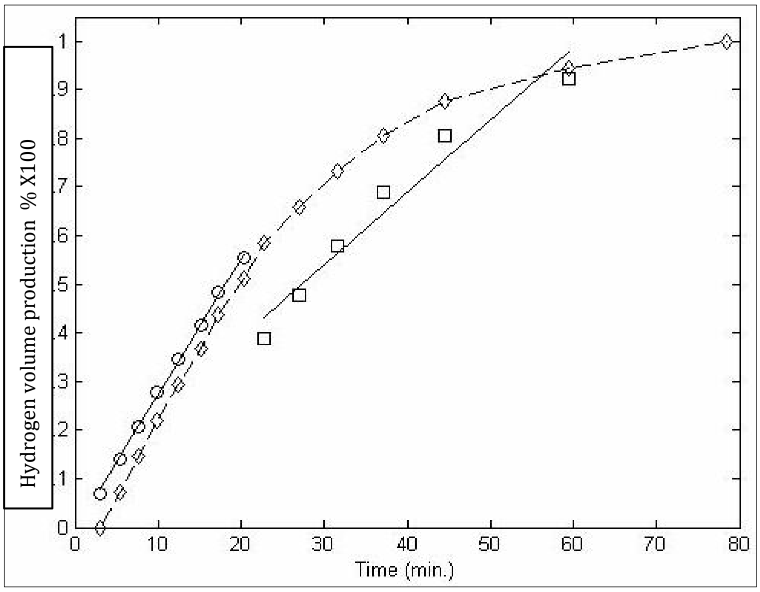
Six commercial aluminium samples were tested. Three from Alutrade, one sample of chopped wire >1mm from a source in Chin, can factory waste from CrownCork, and as a control 99.7% pure aluminium granules >0.25mm supplied by APC Ltd. All except for the APC sample were given various pre-treatments, described here for each sample.

I every case a 50

Sample 1 – Shredded Used Beverage Cans ex Alutrade.

As received these samples were coarsely shredded with a size range between 3mm and 30mm. They were heavily contaminated with mud, fluff, paper, plastic, steel fragments and other unidentifiable foreign matter. This amounted to 6% by weight of the total sample. The can metal was separated from the mass by hand, washed in hot tap water with dish detergent and re-shredded to a uniform 3x2mm then rewashed in hot water to remove mud trapped in the creases and folds now opened up.

The water/hydrogen/aluminium reaction proceeded vigorously and as the graph below shows reaches - in most cases- 90- 95% of the theoretical yield after 80 minutes at 85C. This reaction kinetics curve is absolutely typical for all samples, some react faster at the start of the reaction, some more slowly but 85-95% of the theoretical yield of hydrogen is typically achieved in a small system in 60-80 minutes, but may take as long as 3-4 hours in large or very large systems. Colour of the residual precipitated material was mid-grey, probably due to contamination with can coatings. Washing the insoluble material in two changes of de-ionised water followed by calcination of part of the sample at 750X for just 25 minutes changed this to a pale biscuit-white. Another fraction of the hydroxide sample was retained for LOI testing. See tables at the end of the document for further information.



Sample 2. 'Thermo Swarf', ex Alutrade.

This sample had a range of particle sizes, a maximum of 8x2mm down to >0.25mm. Sample smelt of oil/cutting fluid and contained some foreign matter, including dark-coloured plastic – probably PVC –chips >2mm in size which were removed by flotation when washing and also a few fragments of steel which were removed by a magnet. The reaction produced a creamy-white precipitate with some small specks of unreacted metal and one slightly larger piece which was presumable non-magnetic stainless steel. Hydrogen production was normal and calcining part of the sample produced a near-white sample of aluminium oxide. More data is tabled below.

Sample 3. 2000-7000 Swarf, ex Alutrade.

This sample was of similar appearance and size-distribution to the 'thermo-swarf' sample above but appeared to contain more drill-chippings and fewer turnings. It was also oily and contained quite a few scraps of magnetisable metal and some plastic fragments.. These contaminants amounted to less than 1% of the sample weight and were removed by washing and several passes through a magnetic funnel. Once again a pale biscuit precipitate was produced with a typical rate of hydrogen production. A few specks of unreacted metal were found in the precipitate, >-0.2mm in size, possibly something like anodised aluminium bronze alloy. These disappeared upon calcining, presumably converted to aluminium oxide, but as due to the current pandemic it was not possible to obtain any independent analysis. As in every case LOI tests were carried out on a retained proportion of the precipitate, see tables and other detail below.

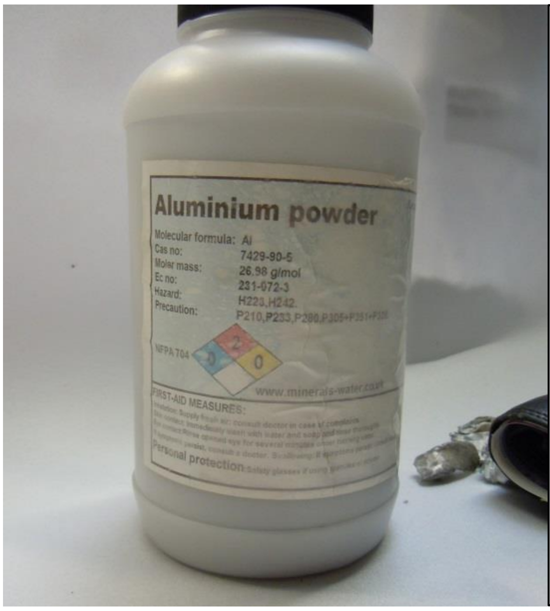
Sample 4. Aluminium shot blasting granules from chopped wire, ex China market

This sample was composed of uniform particles >1mm in size. It was washed once in de-ionised water and dish soap and rinsed before testing. Hydrogen production was slower than the other samples to start with, possibly due to some residual coating of unknown type but soon achieved a similar rate to the rest. The hydroxide precipitate was nearly white in colour and contained no visible metal. For more data see tables below..

Sample 5: Uncoated/coated can punchings ex Crowncork/Ball, S Ireland Plant.

This sample is of can small punchings/trimmings direct from a beverage packing plant. Some were coated with lacquer, some not, though the plant does have the capability to separate these streams at source. They were washed once before use and produced a good flow of hydrogen but a yield only 87% of the theoretical maximum. Upon examination of the precipitate it was discovered that this was due to a small percentage of coated particles that did not react. The hydroxide precipitate was very pale grey but became almost white upon calcining. For more data see tables below.

Sample 6: 99.7% pure aluminium particles: Research grade material.



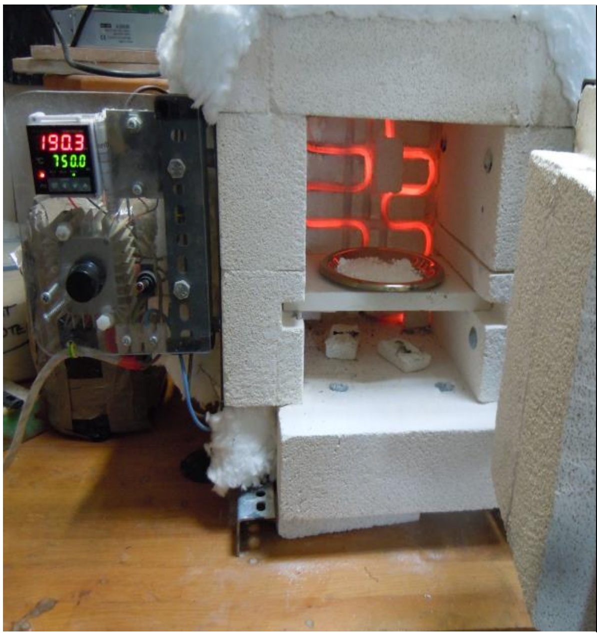
The rationale for testing this pure small-particle material was that it would act as a 'control' for the other tests since it is free from coatings of any kind, plastics, paper, or indeed anything but aluminium. As expected (and previously found) it reacted very vigorously as soon as the catalyst was injected, giving a yield close to the theoretical maximum in only 65 minutes, which is higher than the more typical yield curve for scrap material shown on page 4.

The precipitate was milk-white and contained no unreacted metal particles when examined using a microscope. When calcined this yielded pure white aluminium oxide. A further precipitate sample was dried at 180C and used for LIO testing. For further data see tables below.

SAMPLE NUMBER	%THEORETICAL YIELD	RUN TIME	COMMENTS
SAMPLE 1. UBC ALUTRADE	92	80 mins	Can lacquer flakes only, probable traces of grit from remainder of attached mud etc.
SAMPLE 2. THERMO SWARF	95	80 mins	Yes-pinhead size metallic particles.
SAMPLE 3. 2-7000 SWARF	90	80 mins	Yes- few plastic and tiny metal fragments
SAMPLE 4. AL SHOT BEADS	95	80 mins	None visible
SAMPLE 5. C-CORK CANS	87	80 mins	Yes – pinhead metal fragments and traces of can coating lacquer and/or paint.
SAMPLE 6. PURE AL.	97	80 mins**	None visible

** Run actually ended at 65 mins as reaction had obviously finished.

LOI (Loss On Ignition) Protocol.



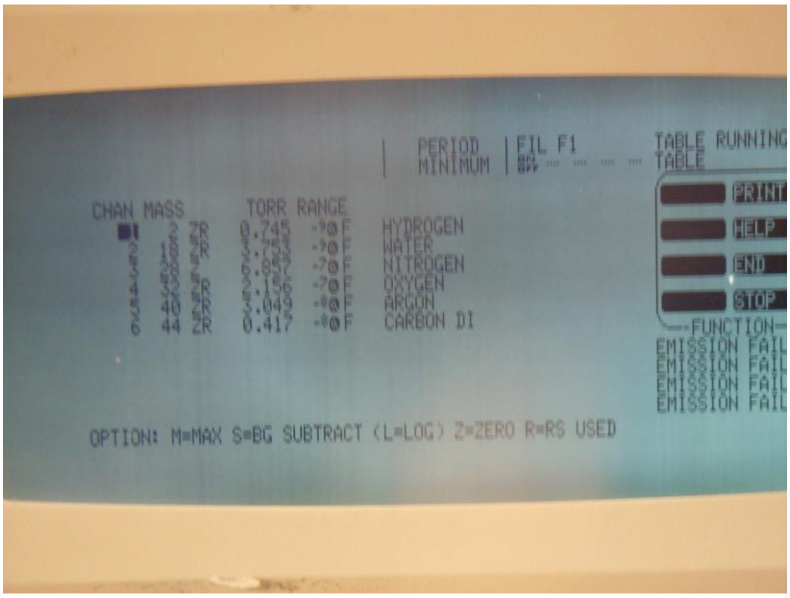
LOI testing is a standard method of determining the hydration state of aluminium (tri) hydroxide Al(OH)3 which is the principal end product of the NetZeroChem method. LOI is carried out using the ASTM D7348 method, in which a weighed sample is first dried at 110C, then reweighed, finally calcined at 1000C and weighed again. This enabled the percentage water lost from a 'dry sample' to be determined after exposure to the higher temperature. The LOI results give an indication of the purity of the hydroxide. We employed (of necessity) slightly modified version of the test in which calcining was carried out at 750C since a 1000C capable kiln was not available. However, 700C+ is normally considered to be adequate for preliminary test purposes.

LOI Test Results

SAMPLE NUMBER	1	2	3	4	5	6
WEIGHT LOSS %*	36.1	35.0****	34.5****	34.4	35.9****	34.5
PURITY % **	94.2***	99.3	99.7	99.6	97.4***	99.7

Notes: * Determined on 50 gr samples, ** Error level +/- 0.3%, *** Figures badly affected by can coating residue lost on calcining, **** Samples screened 100 mesh before testing to remove unreacted metal fragments.

Hydrogen Purity Testing.

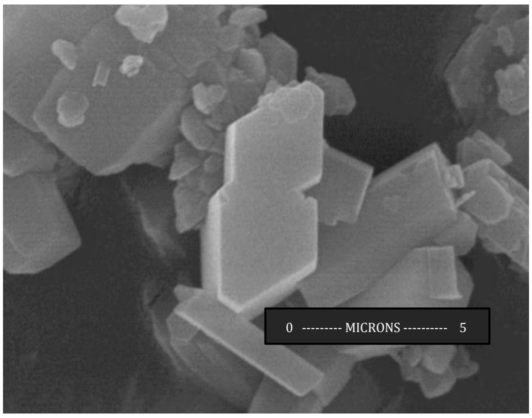


Gas ourity was measured using a Hiden H-100 low molecular weight QMS (quadrapole mass spectrometer) as a gas analyser. This system runs under very high vacuum and gas samples from the test system are bled into the machine via a stainless steel micro-bore tube. Traces of Argon are found and dismissed, since this is used in pure form as a 'carrier gas' and to purge air from the whole system .

SAMPLE NUMBER	1	2	3	4	5	6
IMPURITIES - PPM						
WATER VAPOUR	30	40	52	22	34	44
NITROGEN	12	8	18	9	22	18
OXYGEN	4	3	4	>2	5	4+
CARBON MONOXIDE	0	0	0	0	0	0
CARBON DIOXIDE	1	0	>1	>1	2	1
SULPHUR DIOXIDE	0	0	0	0	0	0
ORGANICS (oils etc)	2	4	>1	0	0	0

It should be noted that the presence of traces of air (oxygen, nitrogen, carbon dioxide) and water vapour are almost impossible to remove from any small low-temperature wet system That is frequently opened for loading and unloading such as the one used. Larger systems will give improved results, but generally this shows that the NetZeroChem method does produce very pure hydrogen very suitable for fuel cells from a varied range of input alloy samples.

Notes on Hydroxide Morphology.



This system produces very uniform 3-5 micron sharp and square-edged particles of aluminium tri-hydroxide as a first product. Unfortunately university and commercial Electron Microscopy and XRF (element analysis) facilities are not available at the moment, this picture is taken from an earlier experiment. This type of hydroxide has very desirable properties as a high value catalyst support material.

Alan Smith, Craig Coates. NetZeroChem Ltd. February/March 2020.