THE SYNTHESIS OF

POTASSIUM ALUMINUM SULFATE (Alum)

FROM ALUMINUM SCRAP

The Chemical Recycling of Scrap Aluminum

This experiment has the following objectives:

1. To be aware of the need for recycling solid wastes, particularly scrap metal like aluminum.
2. To learn some of the chemistry of aluminum.
3. To become familiar with the use of laboratory equipment such as beakers, flasks, Bunsen burners, and so on.
4. To be able to perform the techniques of weighing, gravity and vacuum filtration and crystallization.
5. To be able to apply a knowledge of the stoichiometry of a sequence of chemical reactions to the calculation of the percentage yield of alum synthesized from aluminum scrap.

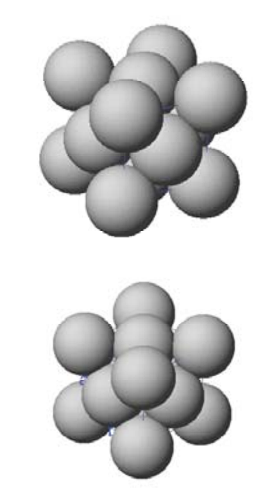

Figure Two views of the unit cell (smallest, repeating unit) of aluminum metal. See the model of aluminum on the Chem Lab page for the course.

INTRODUCTION

Modern societies have concentrated on what might be considered the most primitive of methods of solid waste disposal — burning or burying! This type of behavior is a strange anomaly, because solid waste is probably the oldest of man's pollutants and yet has only recently received serious attention from scientists and technologists.

Like all other environmental problems, solid waste problems are intensified by modern civilization—more people and more things. In 1920 the average American generated 2 3/4 pounds of solid waste per day; in 1970 the average was 5 pounds per day and by 1980 it was about 8 pounds per day! The composition of all this solid waste is shown in the TABLE on the next page; it is drawn from a Public Health Service study of municipal refuse for 1966-1968.

Unfortunately, the problem is compounded by the fact that one of the most important types of resource at the base of our technological society is metal. Metals such as copper, chromium, molybdenum, tin, zinc, tungsten, and aluminum have become as necessary to economics as water and fossil fuels. Aluminum is a classic example!

Aluminum is the third most abundant element, and most abundant metal, in the Earth's crust. It is concentrated in a number of high-grade, natural bauxite deposits, almost all of which are located outside of the U.S. Changes

"Looking at solid waste from the disposal end gives one set of priorities. Looking at solid waste from the standpoint of recycling yields a completely different set of priorities and can illustrate areas of technological need that previously have been overlooked. The salvage of aluminum from mixed municipal refuse is such an area." From Recycling of Used Aluminum Products by Dr. Robert F. Testin.

SOLID WASTE PROFILE—1965 to 1968

Item	*% by Weight*
Paper products	55.0
Glass	7.7
Metals	6.8
Vegetable scraps	2.9
Meat scraps	2.9
Other foods	2.9
Leaves, grass, etc.	10.0
Other	2.8
Adjusted moisture	9.0

in the international situation (the so-called Third World owns most of the bauxite), and the depletion of high grade ores, is forcing the aluminum industry to use lower grade ores with correspondingly higher prices for aluminum and products made from it. At the same time this is happening, the use of aluminum in disposable products (e.g., beverage cans, foil, etc.) is increasing enormously. Even the most solid of all solid wastes, the automobile, now contains more aluminum alloys. The stimuli to recycle aluminum are thus very strong and are being reinforced by other recent developments. The production of aluminum from natural sources like bauxite (aluminum oxide, Al2O3) and cryolite (Na3AlF6) involves an electrolytic process which uses large amounts of electricity. The sky-rocketing cost of that form of energy is well known! The energy costs of recycling aluminum metal, by shredding, melting and casting, are a small fraction (about 5 10%) of the energy cost of producing the metal from ore.

Finally, in an ironic twist, one of the properties of aluminum that is responsible for its current, wide-spread use can cause a serious environmental problem. Aluminum does not corrode as does iron and steel. A fresh aluminum surface reacts very rapidly with oxygen to produce an oxide coating that is so

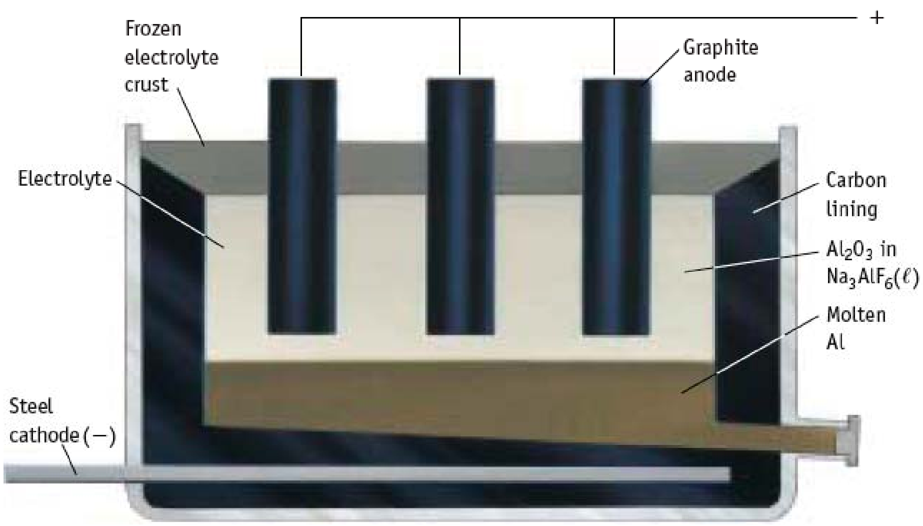

Figure An electrochemical cell used to produce aluminum metal. The aluminum, in the form of compounds such as Al_2O_3 in Na_3AlF_6 is electrolyzed (reduced) at a graphite cathode. Because the cell is at a high temperature, the aluminum is molten, and is drawn off the bottom of the cell. See Chemistry & Chemical Reactivity, 6th edition, page 1035.

tenacious and impervious that no further reaction takes place. The thin layer is not necessary. Hence, skyscraper facings, airplanes, Airstream trailers, and beer cans can be nice shiny objects. The discarded aluminum can has become nearly immortal! It has an average "lifetime" in the environment of greater than 100 years.

There are now a number of successful recycling programs for aluminum cans. Collection centers are paying around 15 cents per pound for scrap aluminum. The problem of recycling cans that end up in the municipal landfill has not yet been solved, but progress is being made in designing large scale separators to separate aluminum, steel, glass, and paper from trash. The scrap aluminum is usually shredded, melted down, cast, and eventually made into an aluminum product.

For a photo of the recovery of aluminum metal from scrap see Figure 21.15(b) in Chemistry & Chemical Reactivity, 6th edition, page 1035.

In this experiment you will be recycling aluminum scrap in a very unusual way, and you will produce two products which are potentially very useful: hydrogen gas (H_2) and very pure potassium aluminum sulfate ($KAl(SO_4)_2{\bullet}12\,H_2O$ or **alum**). Hydrogen gas has great potential use as a fuel, if some of its dangerous properties can be controlled (mixtures of H_2 and air are highly explosive). Hydrogen gas, when burned properly, produces a large amount of heat and no pollution, the only combustion product being water. Alum is a widely used chemical in industry, playing an important role in the production of many products used in the home and industry. The pulp and paper industry alone consumes 70% of the more than one million tons of alum produced annually in the U.S. It is used to "size" the paper. The second largest use is in the purification of water for human and industrial consumption. Other uses include soaps, greases, fire extinguisher compounds, textiles, leather, synthetic rubber, drugs, cosmetics, cement, plastics, and pickles.

Alum is the hydrated compound $KAl(SO_4)_2{\cdot}12H_2O$

It is important to note here that this particular process for converting aluminum into alum would produce very expensive alum! Alum can be made, very cheaply at the moment, using clay as the raw material. Consequently, the procedure used in this experiment is not used as an industrial method for recycling aluminum.

THE CHEMISTRY OF THE EXPERIMENT

Aluminum beverage cans generally have a thin coating of plastic on the inside that protects the aluminum from the corrosive action of the chemicals in the beverage. The outside usually has a thin coating of paint. These coatings must be removed before any chemical reactions with the metal can be carried out. The coatings may be effectively scraped off with a metal pan cleaner. A cleaned piece of metal is then dissolved in a potassium hydroxide solution according to the following complete, balanced equation:

$$2\,Al(s) + 2\,KOH(aq) + 6\,H_2O(liq) \rightarrow 2\,KAl(OH)_4(aq) + 3\,H_2(g)$$

or the net ionic equation

$$2\,Al(s) + 2\,OH^-(aq) + 6\,H_2O(liq) \rightarrow 2\,Al(OH)_4^-(aq) + 3\,H_2(g)$$

The dissolution of Al(s) in aqueous KOH is an example of an **oxidation-reduction** or **redox** reaction. [The Al metal is oxidized to aluminum with an oxidation number of +3 and the hydrogen in KOH or in water is reduced from an oxidation number of +1 to zero in hydrogen gas.] The $Al(OH)_4^-$ ion is a complex ion called "aluminate." These reactions illustrate the reason that alkaline products (such as detergents, cleaners, shampoos, and so on) are never stored in an aluminum container. The aluminum would slowly dissolve!

After filtration to remove residual plastic and paint decomposition products, the alkaline solution of $Al(OH)_4^-$ is **clear** and **colorless**. The H_2 is evolved as a gas and mixes with the atmosphere. The chemical species in solution are potassium ions (K^+) and aluminate ions [$Al(OH)_4^-$] ions (plus any unreacted KOH).

Sulfuric acid is now added and two sequential reactions occur. Initially, before the addition of all the acid, the complete reaction is

$$2\ KAl(OH)_4(aq) + H_2SO_4(aq) \rightarrow 2\ Al(OH)_3(s) + 2\ H_2O(liq) + K_2SO_4(aq)$$

or the net ionic equation

$$Al(OH)_4^-(aq) + H^+(aq) \rightarrow Al(OH)_3(s) + H_2O(liq)$$

The reaction above is an acid-base reaction in which the H^+ ions from the sulfuric acid neutralize the base $Al(OH)_4^-$ to give a thick, white, gelatinous precipitate of aluminum hydroxide, $Al(OH)_3$.

Note that "**clear**" and "**colorless**" describe two different things. The word "clear" means that the solution is free of suspended matter, that is, it is not cloudy and light can pass cleanly through the solution without being scattered. "Colorless" means that the solution is without color. Thus, it is possible for a solution to be colorless but not clear (it would appear white), colorless and clear (pure water), or clear and colored (beer).

As more sulfuric acid is added, the precipitate of $Al(OH)_3$ dissolves.

$$2\ Al(OH)_3(s) + 3\ H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6\ H_2O(liq)$$

or the net ionic equation is

$$Al(OH)_3(s) + 3\ H^+(aq) \rightarrow Al^{3+}(aq) + 3\ H_2O(liq)$$

to give aluminum ions, Al^{3+}, in solution. The solution at this point contains Al^{3+} ions, K^+ ions (from potassium hydroxide), and SO_4^{2-} ions (from sulfuric acid). On cooling, crystals of **hydrated** potassium aluminum sulfate, $KAl(SO_4)_2 \bullet 12\ H_2O$ (or alum) are very slowly deposited. In the experiment the crystallization process is speeded up by providing a small "seed crystal" of alum for the newly forming crystals to grow on. Cooling is needed because alum crystals are soluble in water at room temperature. The complete equation is

$$Al_2(SO_4)_3(aq) + K_2SO_4(aq) + 24\ H_2O(liq) \rightarrow 2\ KAl(SO_4)_2 \bullet 12\ H2O$$

and the net ionic equation is

$$K^+(aq) + Al^{3+}(aq) + 2\ SO_4^{2-}(aq) + 12\ H_2O(liq) \rightarrow KAl(SO_4)_2 \bullet 12\ H_2O(s)$$

In the formula for alum—$KAl(SO_4)_2 \cdot 12H_2O$—twelve molecules of water are written after a period to indicate that the water is incorporated in the crystal structure as water of crystallization. Such compounds are often called **hydrated compounds**.

Finally, the crystals of alum are removed from the solution by vacuum filtration and washed with an alcohol/water mixture. This wash liquid removes any contamination from the crystals but does not dissolve them. It also helps to dry the crystals quickly, because alcohol is more volatile than water.

EXPERIMENTAL PROCEDURE

• Bring an aluminum can to laboratory.

• WEAR YOUR SAFETY GLASSES.

1. Clean all glassware.
2. Pierce the can at the lower end of the side with the point of a pair of scissors. Cut around so that the sides of the can are cut out. Deposit the waste aluminum scraps left over in the box provided.
3. Lay the rectangular piece of aluminum (the sides of the can) on the bench and scour both sides with the pan scrubber provided. Make sure that an area of 2" x 2(1/4)" is clean on both sides.
4. Wipe the metal clean with a paper towel and cut out a clean piece that is about 2" x 2 1/4".
5. Take this piece to the analytical balance and weigh it. If the piece weighs

more than 1 g, cut small pieces off until it weighs about 1 gram. Now weigh the piece accurately, and ***record the mass on your report form.***

6. Cut the weighed piece into smaller pieces, and place them a clean 250 mL beaker. Do not lose any metal bits.
7. Using a graduated cylinder, add 50 mL of 1.4 M KOH. **DO IT IN THE HOOD!**
8. Set up a ring stand, ring clamp, gauze, and bunsen burner. Place the beaker on the gauze and heat the beaker on a low flame. It is not necessary to boil it. The aluminum will take about 20 minutes to dissolve.
9. While it is dissolving, set up an apparatus for ***gravity filtration*** (as described by the figure on page A-3). Place a clean funnel, with a piece of folded filter paper, on a 125 mL Erlenmeyer flask.
10. When the aluminum has dissolved (as evidenced by the lack of bubbles of H_2 gas given off), gravity filter the solution. Only fill the funnel to within 1/2" of the top of the paper. Use a glass rod to "guide" the solution into the paper (as demonstrated by your instructor). The solution in the Erlenmeyer flask should be both clear and colorless at this point.
11. Allow the flask to cool. While it is cooling, wash the funnel and beaker with lots of tap water to remove any potassium hydroxide.
12. When the solution is reasonably cool, add 20 mL of 9 M H_2SO_4 (with a graduated cylinder) quickly and with care. It is important that you swirl the flask as you add the acid. The solution will get quite warm. If there are any white flecks left in the solution after the addition of the H_2SO_4, place the flask on the Bunsen burner apparatus and warm it with swirling until all of the solid material has dissolved.
13. Make an ice bath by putting ice and water into a 600 mL beaker.
14. Allow the flask to cool a little and then place it in the ice bath and allow it to cool for an additional 5 minutes.
15. If alum crystals have not started to form, scratch the inside walls of the flask with a stirring rod. This provides sites at which crystallization can begin, followed by crystal formation throughout the liquid. Swirl the flask when you notice the onset of crystal formation and allow it to cool in the ice bath for another 10 minutes.
16. While the solution is cooling, pour 50 mL of 50% alcohol/water mixture into a test tube and place it in the ice bath to cool.
17. Set up the ***vacuum filtration*** apparatus (Buchner funnel) as illustrated by your instructor and on the following page. Pour some distilled water onto the filter.
18. Remove the flask containing the alum crystals from the ice bath, swirl so that all the crystals are dislodged, and pour quickly into the Buchner funnel. Keep swirling and pouring until all the solution and crystals are transferred to the funnel. The water aspirator should be kept going all through this process.
19. Pour about 10 mL of the cooled alcohol/water mixture into the flask. Swirl the flask and pour mixture into the funnel to transfer any remaining crystals.

PLEASE DO NOT LEAVE A MESS AROUND THE BALANCE AREA!

Don't try to bring the mass to exactly 1.000 g. You can use 0.956 g or 1.025 g, for example.

(BE CAREFUL with the KOH solution. It will dissolve aluminum and you!

For the procedure on **gravity filtration**, see the Crystal Growing experiment, page A-3.

Use great caution in handling 9 M sulfuric acid. It is very corrosive.

Step 1: You need a glass or plastic filter flask (with sidearm), a plastic or porcelein funnel, and a piece of filter paper.

Step 2: Clamp the filter flask onto your ringstand so theflask will not tip over. Attach a piece of rubber vacuum tubing.

Step 3: At the other end of the vacuum tubing make sure there is a little plastic fitting.

Step 4: Plug the vacuum tubing with the plastic fitting onto the water spigot in front of your lab station. Turn on the water all the way and test to see if a vacuum has been createds in your flask and funnel.

Figure This figure illustrates the way to set up and carry out a vacuum filtration.

20. Wash the alum crystals, now on the filter, with the cooled alcohol/water mixture using the following procedure: Disconnect the aspirator hose from the aspirator unit on the faucet. Pour about 5-10 mL of alcohol/water onto the crystals and gently stir. Reconnect the aspirator hose, and suck the crystals dry. After pouring on the last portion of alcohol/water suck the crystals dry for at least 20 minutes.
21. Place the nearly dry alum crystals in the evaporating dish in your desk until the next laboratory period.
22. In the next period accurately weigh your yield of crystals, recording the weight of product on the report form.
23. After weighing your alum sample ***(make sure you have recorded the mass)***, place the sample in your large test tube and hand it in to your instructor. Make sure that your test tube is labeled with your name and lab section number.

Make sure you have recorded the mass of your alum on your report form. Be sure you give your sample, in a labeled, large test tube, to your instructor before you leave the laboratory.

CALCULATIONS

The objectives of this experiment are:

a) to prepare a sample of alum from aluminum scrap, and

b) to perform some stoichiometry calculations, specifically the percent yield of product.

The stoichiometry involved in the sequence of reactions leading to the preparation of alum provides the mole relationship between aluminum and alum that is required to calculate the percentage yield.

$$2\ Al(s) + 2\ KOH + 6\ H_2O \rightarrow 2\ K[Al(OH)_4] + 3\ H_2 \quad (1)$$

$$2\ K[Al(OH)_4] + H_2SO_4 \rightarrow 2\ Al(OH)_3(s) + 2\ H_2O + K_2SO_4 \quad (2)$$

$$2\ Al(OH)_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\ H_2O \quad (3)$$

$$Al_2(SO_4)_3 + K_2SO_4 + 24\ H_2O \rightarrow 2\ KAl(SO_4)_2{\bullet}12H_2O \quad (4)$$

$$2\ Al(s) + 2\ KOH + 4\ H_2SO_4 + 22\ H_2O \rightarrow 2\ KAl(SO_4)_2{\bullet}12H_2O + 3\ H_2 \quad (5)$$

MOLAR MASSES

Al, 26.98 g/mol

KAl(SO4)2•12H2O, 474.39 g/mol

The **overall reaction** for the synthesis of alum, equation (5), is obtained by adding reactions (1-4) and canceling like-species. The overall reaction stoichiometry (5) informs us that 2 moles of aluminum will produce 2 moles of alum.

Your *calculations* should proceed as follows:

a) Calculate the number of moles of Al used from the mass of Al used.

b) Knowing that the stoichiometric factor is

$$\text{Stoichiometricfactor} = \frac{2\ \text{mol}\ KAl(SO_4)_2 \cdot 12H_2O}{2\ \text{mol Al}}$$

calculate the quantity of alum ($KAl(SO_4)_2{\bullet}12H_2O$), in moles, that should be produced theoretically from the quantity (in moles) of aluminum metal used. Enter this calculation on your report form.

c) Knowing the number of moles of $KAl(SO_4)_2{\bullet}12H_2O$ expected, calculate the mass of $KAl(SO_4)_2{\bullet}12H_2O$ expected (the ***theoretical yield***). Enter this on your report form.

d) Calculate the ***percentage yield*** of alum, if

$$\%\ \text{yield} = \frac{\text{mass of alum obtained (g)}}{\text{mass of alum theoretically obtainable (g)}} \times 100\%$$

Enter the result of your percent yield calculation on your report.

Give the completed report form to your laboratory instructor by the indicated due date. Be sure that your instructor also has the sample of the alum that you prepared.

SYNTHESIS OF POTASSIUM ALUMINUM SULFATE

Name ____ Section ________ Grade ______

EXPERIMENTAL DATA

Mass of aluminum used _____________________________

Mass of paper or beaker + $KAl(SO_4)_2{\bullet}12H_2O$ ____________________

Mass of paper or beaker ____________________

Mass of $KAl(SO_4)_2{\bullet}12H_2O$ ____________________

CALCULATIONS: *Show your calculations throughout!*

1. How many moles of aluminum metal did you use?

2. Assuming that Al metal is the limiting reagent, what quantity of potassium aluminum sulfate (alum), in moles, is theoretically obtainable?

3. What mass of potassium aluminum sulfate (alum, $KAl(SO_4)_2{\bullet}12H_2O$), in grams, is theoretically obtainable from your mass of Al? That is, what is the ***theoretical yield*** of alum?

4. What was the ***percentage yield*** of your product, $KAl(SO_4)_2{\bullet}12H_2O$?