



Review

Improving aluminum recycling: A survey of sorting and impurity removal technologies

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ABSTRACT

Aluminum recycling has a number of key environmental and economic benefits. With these energy and cost savings in mind, many producers now have targets of increasing their usage of secondary materials. However, the accumulation of impurities in these recycled material streams may provide a significant compositional barrier to these goals. A growing number of studies and literature suggest that accumulation of unwanted elements is a growing problem; for the case of aluminum, the list of problematic impurities is quite large, including but not limited to Si, Mg, Ni, Zn, Pb, Cr, Fe, Cu, V, and Mn. The removal of unwanted elements in the scrap stream is dictated by the energy considerations of the melt process. Compared to many metals, it is challenging to remove tramp elements from aluminium. Therefore, with no simple thermodynamic solution, producers must identify strategies throughout the production process to mitigate this elemental accumulation. There are a variety of solutions to deal with accumulation of undesired elements; each presents a trade-off between cost and efficacy (tramp removal). Dilution with primary is the most common solution used in industry today; this has a negative impact on recycling as the required dilution results in a compositionally determined cap to recycling rates. This article provides an overview of the expanse of upgrading technologies available at both the industrial and lab-scale to improve aluminum scrap purity and facilitate recycling.

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1. Motivation

Aluminum recycling has a number of key environmental and economic benefits. Compared to other high volume materials, aluminum production has one of the largest energy differences between primary and secondary production: 186 MJ/kg for primary compared to 10–20 MJ/kg for secondary (Green, 2007). With energy and cost savings in mind, many producers now have targets of increasing their usage of secondary materials (2002; Alcoa, 2006). However, the accumulation of impurities in these recycled material streams provides a significant, long-term compositional barrier to these goals (Liu, 2003).

A growing number of studies and literature suggest that accumulation of unwanted elements is a growing problem, in all recycled material streams. In the case of aluminum, the list of problematic impurities is quite large, including but not limited to Si, Mg, Ni, Zn, Pb, Cr, Fe, Cu, V, and Mn (Kim et al., 1997; Viklund-White and Menad, 1999; Gesing, 2004; Lundqvist et al., 2004; Das, 2006; Gesing and Harbeck, 2008; Gaustad et al., 2010). Metal recycling is a metallurgical process and is therefore governed by the laws of thermodynamics. The removal of unwanted elements in the scrap stream is dictated by the energy considerations of the melt process. Compared to many metals, aluminum presents a high degree of difficulty in the removal of tramp elements, due to thermodynamic barriers as detailed in Section 3. Therefore, with no simple thermodynamic solution, producers must identify strategies throughout the production process to mitigate this elemental accumulation.

There are a variety of solutions to deal with the negative impact on recycling due to accumulation of undesired elements; each presents a trade-off between cost and improvement in scrap utilization (or recycling) potential. Dilution with primary is the most common solution used in industry today; this has a negative impact on recycling as the required dilution results in a compositionally determined cap to recycling rates. “Down-cycling”, where materials are recycled into lower value products, is another common method of dealing with contaminated secondary materials; this enables higher usage of recycled materials but negatively effects recycling economics. A specific example of down-cycling is when wrought scrap is used in cast products due to their ability to accommodate higher silicon contamination. As important as these operational strategies are to mitigating the negative effects of accumulation, there are far more technological strategies available to the producer when these operational strategies become ineffective. This article aims to provide an overview of these upgrading technologies, categorized by the main mechanism in which they remove unwanted elements either by (1) physically separating solid scrap streams to prevent co-mingling of metals and elements or (2) refining technologies that attempt to chemically or kinetically move unwanted particles and elements in the melt.

2. Pre-melt technologies: physical separation

While physical separation technologies can be applied to a wide range of scrap streams, they are typically used for scrap that has been shredded (Wilson et al., 1994). The majority of automotive scrap, for example, goes through some sort of shredding process before being sold to secondary re-melters. These automotive hulks will be a focus of many of the upgrading technologies as they

make up a large portion of end-of-life recycled scraps (Kelly and Matos, 2010). There are approximately 200 shredders operating in North America; most use large hammer mills to smash scraps such as end-of-life automotive hulks into pieces typically smaller than four inches (Rousseau and Melin, 1989). Before using some of the more advanced physical separation technologies described below, general separation by particle size is often applied using various screening methods. De-lacquering processes are also quite common in which the scrap is heated to remove paints, paper and plastic labels, and other coatings.

2.1. Magnetic

Magnetic separation is a way to separate the non-ferrous and ferrous scrap components. Typically, a conveyor belt with the scrap materials is fed near another conveyor belt equipped with NdFeB magnets. As the scrap nears this magnet, the ferromagnetic portion (mainly steel and some iron) is attracted to the magnet and pulled onto the second conveyor belt while the non-ferrous portion falls into a collection bin. This technology is used extensively in the secondary aluminum industry. Its main limitations are that further separation of the non-ferrous scrap stream is not possible and it may still contain many contaminating portions that are not magnetic such as plastic, glass, rubber, stainless steel, copper, zinc, magnesium, etc.

2.2. Air separation

Technologies using air to separate scrap streams are known by many different names: windsifting, air-knives, elutriation, winnowing, air columns, etc. Their differing names refer to the slightly different mechanisms by which they work. Conveyor belt systems often use suction to pull off light-weight materials present in shredded automobiles such as plastic, rubber, and foam. These lightweight components are often referred to as “shredder residue” and are usually landfilled (Gesing, 2001). In a vertical air separation system, the recycled material stream is fed through a column with air pushing upwards; the heavy metals are collected at the bottom and the other materials are pushed through various feeds further up. Most secondary remelter facilities will use some sort of air separation technique to create a mostly metallic scrap stream. The main drawback is the loss of lightweight metallic products such as used beverage cans and shredded pieces that are of a smaller size (Veasey et al., 1993).

2.3. Eddy current separation

Initially developed to sort aluminum cans from household wastes, the use of eddy currents soon became standard industry practice for further separation of non-ferrous automotive shredder residue. Eddy current separation takes advantage of the large range in conductivities of many of the mixed metals present in co-mingled automotive (and other) scraps (Table 1). Eddy current separation is a similar concept to magnetic separation. A rotor is lined with NdFeB magnets with alternating north and south poles. The rotor produces an external magnetic field which repels nonmagnetic electrically conductive metals; this results in their expulsion from the scrap stream, leaving the non-metallic particles. The magnetic field can be controlled with the speed of

Table 1
Electrical conductivity of several metals.

Electrical conductivity ($\times 10^6 \Omega \text{ cm}^{-1}$)		Electrical conductivity ($\times 10^6 \Omega \text{ cm}^{-1}$)	
Mn	0.006	Fe	0.093
Sb	0.028	Ni	0.143
Pb	0.048	Zn	0.166
Al	0.067	Mg	0.226
Cr	0.077	Cu	0.596
Fe	0.093	Ag	0.630
Ni	0.143		

Table 2
List of automotive scrap component categories and typical density ranges (Callister, 2000).

Scrap components	Density (g/cm ³)
Lead	10.8–11.0
Copper	8.0–9.0
Brass and bronze	5.0–7.0
Stainless steel	7.6–8.0
Zinc	5.5–7.2
Aluminum	2.6–2.9
Magnesium	1.7–1.9
Plastics	0.9–1.5
Rubber	0.8–0.9
Foams	0.01–0.5

the rotor. The eddy current (i) generated in a scrap metal can be given by:

$$i = \frac{(K * v * B) * \sigma * A}{L} \quad (1)$$

where A is the cross-sectional area, L is the thickness, σ is the conductivity, B is the magnetic field flux density, v is the frequency of oscillation, and $(K * v * B)$ is the potential difference across a scrap fragment (Kercher and Webb, 1982). Because this technology relies on the magnetic repulsion force to be generated within the material, some shapes such as wires and foils fail to be separated out as they do not produce a sufficient eddy current. Applications of this technology to further separate the non-ferrous components have been reported (Gesing, 2001). The extension of this technology takes advantage of the fact that metals with varying conductivity will produce varying eddy currents and will therefore be thrown different distances. By setting up collection bins at these varying distances from the rotor, it is possible to separate the scrap stream by base metal.

2.4. Sink float/heavy media separation

Sink float separation uses water-based slurries with known specific gravity to separate non-ferrous materials with differing densities. For example, in the case of a shredded automotive scrap stream, many of the components have different densities (Table 2), which makes it an excellent application of this technology. Fine particles are first screened out of the process; these are often landfilled or shipped to hand sorting facilities. For a typical three step process, the resulting coarse fraction starts in a water bath (specific gravity of one), which enables separation of much of the non-metallic fraction (plastics, foams, wood, etc.). Next, a 2.5 specific gravity-bath separates magnesium and higher density plastics. To control the specific gravity of the bath, magnetite or ferrosilicon powder is added. The third bath has specific gravity of 3.5 and separates the cast and wrought aluminum metals out leaving behind heavier metal components such as copper, zinc, and lead. Some drawbacks of this technology include the high cost of maintaining the constant density slurries as well as the loss of hollow or boat-shaped metal components.

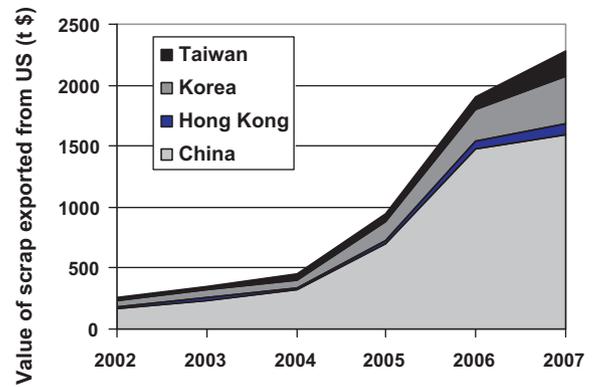


Fig. 1. Value of US scrap exports by country (Plunkert, 2010).

Fluidized bed sink float technology is also in development; this is a dry technique using a bed of sand and forced airflow through the bed. By changing the speed of the airflow one can control the density of the sand and therefore separate different density scraps without transferring them to different liquid baths. Problems with lubricants on the scraps and difficulties in controlling convection currents have prevented this technology from commercialization.

2.5. Color sorting – by hand and spectrographic technologies

Color sorting takes advantage of the color difference between scraps to separate zinc, copper, brass, and stainless steel from aluminum in a non-ferrous scrap stream. The most basic application of color sorting is when metals are sorted by hand, a prevalent practice in countries with low labor costs. United States exports of scrap to these countries have been growing substantially in recent years (Fig. 1); the value of scrap exported to Taiwan, Korea, Hong Kong, and China has grown fivefold in five years. Empirical evidence of the capabilities of hand sorting beyond observation have not been reported; however, it is estimated that workers in China can achieve accuracies up to 99% when sorting non-ferrous automotive shred (Minter, 2006). Because of distinctive surface characteristics that differ between them, it has also been cited that hand sorting is capable of sorting wrought and cast aluminum fractions (Rao, 2006).

Color sorting can also occur through automated processes. A computer analyzes images of each scrap and, based on specified color ranges, directs them to different feeds. The technology is not impacted by the particle size or shape of the scraps so it has many capabilities lacking in heavy media and eddy current separation. To further separate non-ferrous metallic fractions, chemical etching is often used in conjunction with color sorting. This technology has the capability to separate aluminum by alloy family. For example, copper sulfate dissolved in hydrochloric acid etchant enables a color sorter to identify 5XXX and 6XXX series (magnesium containing) alloys (Schultz and Wyss, 2000). Other etchants such as sulfuric acid will color high silicon and manganese alloys a light gray color while zinc and copper containing alloys will turn a darker color enabling separation of 2XXX, 3XXX, and 7XXX series alloys (Schultz and Wyss, 2000). Two key barriers remain to widespread use of this method, however, (1) the environmental and economic impact of the etching chemicals, and (2) surface roughness (resulting from use) and the effect of heat treatments done in processing can greatly impact the resulting color of the scraps and therefore final identification and separation.

2.6. Other spectrographic techniques

Spectroscopy has become more widely used for identification and sorting of aluminum and magnesium alloys in recent years. In this technology, various scrap pieces pass by an array of sensors which trigger one of three main activation methods: (1) X-rays, (2) neutron flux, and (3) pulse laser. The relevant source hits the metal which produces an emission: X-ray fluorescence by the X-rays, gamma ray fluorescence by the neutron flux, and an optical emission for the pulse laser. These spectra are read by varying types of detectors and a computer then sends a signal that sends the piece of scrap to the appropriate bin. Hand-held X-ray fluorescence (XRF) units are currently in use, but their high cost prevents pervasive use in scrap processing yards. For XRF, the spectral ratios of scrap materials are determined according to their major alloying element because aluminum has a very low characteristic radiation which cannot be read unless under vacuum. Studies on the commercial applicability of XRF in sorting have shown it to be capable of separating by major alloy family but cannot determine specific alloys (Krotkov et al., 1993). Neutron activation requires long exposure times to the neutron flux due to its limited intensity and therefore has not been commercialized.

One technology in particular, laser induced breakdown spectroscopy (LIBS), which utilizes a pulse laser and optical emission spectroscopy, has shown great promise for sorting of wrought and cast aluminum (Gesing et al., 2003a). LIBS was first developed by Los Alamos National Laboratory; its first application to composition identification of metallic scrap pieces was in 1990 in a joint project with Metallgesellschaft, formerly a large mining and engineering company based in Germany (Sattler, 1990; Sattler and Yoshida, 1993). In this method, a sensor detects a piece of scrap material which activates a pulse laser. The laser hits the surface of the metal and produces an atomic emission. The optical spectra are read by a polychromator and a photodiode detector which sends a signal to a computer system (Gesing et al., 2001a). The system can then direct the piece of scrap to an appropriate bin using a mechanical arm. Another system under development utilizes an air table; where the detector sends a signal which triggers a burst of air beneath the scrap metal thus ejecting it into the correct container. LIBS has many advantages over current separation technologies for both automotive and aerospace applications as it has the possibility for high speed and high volume. It has capabilities to separate wrought and cast alloys and to sort wrought alloys by alloy family (Gesing et al., 2002, 2003a). However, some drawbacks to commercial use remain however. Pulse lasers can only penetrate a small distance into the surface of a metal, and therefore the scrap must be free of lubricants, paint, and other coatings. Even when the scrap is clear of these, oxide formation on the surface could cause erroneous readings. Regardless, this technology has been gaining ground, especially in automotive applications (Gesing and Harbeck, 2008).

2.7. Hot crush

The hot crush process is a thermal-mechanical separation method that is currently one of the few ways to successfully separate wrought and cast aluminum alloys in industry. This process takes advantage of the low eutectic temperature of cast alloys, which are high in silicon. Because the cast alloys have a lower melting temperature than the wrought alloys, holding or “soaking” the mixed scrap at a temperature below the eutectic ($\sim 550^\circ\text{C}$) will result in a weakening of the castings along their grain boundaries. A subsequent mechanical crushing or grinding then causes those alloys to break and they can be separated from the wrought with various particle size screening processes. A positive side effect of the heating phase is that painted scrap also experiences some

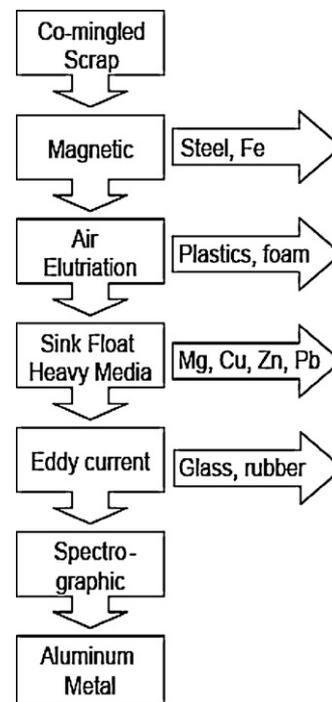


Fig. 2. Diagram of possible physical separation sequence for co-mingled scrap, particularly automotive.

delacquering. Studies have shown the technology to be 96% effective in separating a mixed wrought–cast stream (DeGaspari, 1999). However, successful segregation requires that the initial scraps be fairly large in size as the screening portion relies on the wrought aluminum remaining that way. Therefore, separation of shredded scrap streams or smaller products is not possible.

2.8. Summary of physical separation technologies

Often, particularly in the case of shredded automotive hulks, co-mingled scrap will be subjected to a variety of these physical separation technologies to achieve a relatively pure aluminum scrap stream for melting. The technologies used and their use sequence varies between different secondary producers and scrap processors. A typical physical separation sequence is shown in Fig. 2.

3. Melt technologies: refining

Once scrap material enters the furnace, physical separation technologies can no longer be applied. Technologies aimed at removing impurities from the melt are quite prevalent. Melting is a metallurgical process and is therefore governed by the laws of thermodynamics. The removal of unwanted elements in the scrap stream is dictated by the energy considerations of the melt process. In the case of aluminum, the thermodynamic barrier to the removal of most elements is quite large. Fig. 3 shows an Ellingham diagram for alumina reduction illustrating the Gibbs free energy change as a function of temperature for various oxidation reactions. The main reaction of note, reduction of alumina to aluminum metal as expressed in Eq. (2), is the thick black line in the middle of Fig. 3. One can see that the majority of equilibrium lines are at a higher free energy than aluminum, indicating that no partial pressure of oxygen would allow them to be oxidized into the slag. Of the elements shown here, only magnesium and calcium can be effectively removed from the melt by simple oxidation. In the case of iron and by extension, steel as shown in Fig. 3, only copper and nickel have a

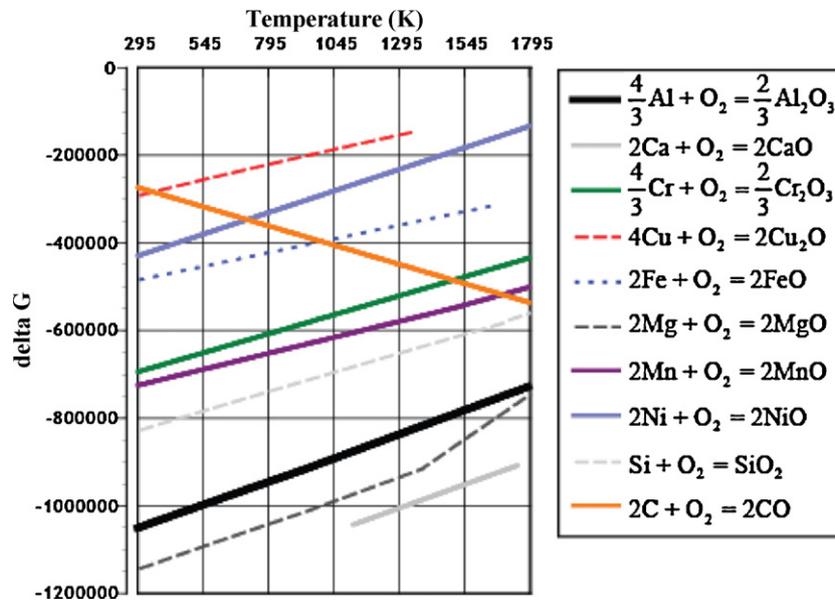


Fig. 3. Ellingham diagram for various reactions (Kubaschewski et al., 1979; Ragone, 1995).

Table 3
Melting temperature of several metals.

	Melting temperature	
Tin (Sn)	232 °C	449 °F
Lead (Pb)	327 °C	621 °F
Zinc (Zn)	419 °C	787 °F
Aluminum (Al)	660 °C	1220 °F

higher free energy than iron oxide reduction and therefore all other elements listed can be efficiently removed from the melt.



Selective melting, or “sweating”, is often performed to separate contaminating metals that have not been removed by physical separation techniques; particularly when metal parts are welded together. When sweating, a reverberatory or rotary furnace is used and the temperature is stepped and held at different intervals to take advantage of contaminating metals with lower melting temperatures than aluminum (Table 3). The unwanted melted materials can then be easily removed prior to melting down the aluminum portion.

3.1. Fluxing

The most common technology aimed at removing impurities from the melt is simple fluxing. Fluxing is when various compounds (usually inorganic salts), chemicals, and gases are added to: (1) reduce oxidation, (2) encourage certain elements to migrate into the dross, or top layer of the melt, (3) increase the fluidity or wettability of the melt which facilitates the separation of inclusions, (4) remove hydrogen and nitrogen gas, and (5) remove Ca, Sr, Na, Mg, and Li (Utigard et al., 1998). Fluxes are useful in removing calcium, magnesium, sodium, etc. from aluminum by serving as catalysts for their equilibrium oxidation reactions (cf. Fig. 3). They will form more stable chlorides and fluorides than aluminum which can then be removed from the melt through sedimentation or dross formation depending on their resulting density. For example, addition of AlCl_3 will cause the following reaction: $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$. MgCl_2 has a lower density than liquid aluminum and will migrate to the dross. The most common solid fluxes in use include KCl, NaCl, NaF, AlF_3 , and MgCl_3 and common fluoride salt additions such as

Na_3AlF_6 (cryolite), CaF_2 , and Na_2SiF_6 (Utigard et al., 1998). Many of the fluoride fluxes are capable of slightly dissolving thin oxide films and therefore expose aluminum metal improving the metallic yield. While the use of fluxes is prevalent in secondary aluminum processing, there are still several drawbacks. One limitation is that a large amount of flux may be required to achieve efficient reactions. For example, studies estimate that for a 100% efficient reaction, 2.95 kg of chlorine would be required to remove 1.0 kg of magnesium. Therefore, for a typical wrought 5XXX or 6XXX series scrap melt, it would require up to 120 kg of chlorine gas to remove the magnesium from one metric ton of aluminum (Utigard et al., 1998). Also, chlorides and fluorides produce toxic and dangerous gases which must then be filtered from emissions.

3.2. Hoopes process

Certain applications of aluminum metal, such as foil for capacitors and disk blanks, require extremely low levels of impurity elements and inclusions. Often, primary aluminum will have levels of silicon and iron that are too high for these applications due to pick-up from stirring equipment and the furnace refractories. Therefore, the production of high purity aluminum (>99.97% or 3N7) requires various refining technologies and these technologies can remove accumulated tramp elements from scrap melts as well. A common refining technology is a three-layer process referred to as the Hoopes process. The three density separated layers consist of an aluminum copper alloy on the bottom which serves as the anode, a layer of molten electrolyte, and the top layer of molten purified aluminum. The scrap aluminum is added to the anode layer and purifies as it is electrolytically transported to the cathode layer because the other elemental impurities will not migrate. The three-layer electrolytic process requires high temperatures (700–900 °C) and is very energy intensive (17–18 kWh/kg). As primary production requires approximately 14 kWh/kg, it is therefore only appropriate for extremely high purity production (Kondo et al., 1990).

3.3. Low temperature electrolysis

Low temperature (~100 °C) electro-refining methods have been shown to produce aluminum of 99.89% purity (Kamavaram et al.,

2003). The lower temperature electrolysis can provide significant energy savings over the Hoopes process. For this, anhydrous aluminum chlorides are used to form an ionic liquid; the aluminum that needs to be refined is placed in this solution and becomes the anode. The purified aluminum is electrodeposited on a pure aluminum or copper cathode according to the following electrochemical reactions: (1) Al alloy (anode) + 7AlCl₄⁻ → 4Al₂Cl₇⁻ + 3e⁻ and (2) 4Al₂Cl₇⁻ + 3e⁻ → pure Al (cathode) + 7AlCl₄⁻. This electrolysis is capable of removing Mn, Fe, Si, Cu, Zn, Ni, and Pb (Kamavaram et al., 2003). Because the ionic liquids are stable at the lower operating temperature, they can be reused thus making the process more environmentally friendly.

3.4. Segregation

Segregation processes fall into two categories: unidirectional solidification and fractional crystallization (Kondo et al., 1990). Unidirectional solidification, also referred to as zone melting, is still in the research and development phase and has shown promise for purifying bars of aluminum metal (Sillekens et al., 2000). By tightly controlling melting and re-solidification of the metal, the technology forces unwanted impurity elements to migrate or concentrate in one region. This is accomplished by slowly pulling a bar of aluminum metal through a ring-shaped furnace, creating a traveling molten zone in the bar. As the bar cools, purified crystals of aluminum will form and the impurity elements will remain in the molten zone. The pulling rate controls the speed of recrystallization and, therefore, the degree of purity of the re-solidified portion (Rao, 2006). The impurity elements can then be condensed in the end of the sample bar and this portion may be removed. Zone melting has a lower refining ratio than fractional crystallization but some studies suggest it may be better suited to mass production (Rao, 2006).

The fractional crystallization refining process is typically used to remove impurities from primary aluminum in order to produce very high purity aluminum (>99.97% or 3N7). Fractional crystallization provides cost savings compared to both three-layer electrolytic refining and zone refining (Kahveci and Unal, 2000). The Alcoa fractional crystallization method has been shown to produce aluminum of 3N7 to 6N quality; typical applications include memory disks, capacitor foil, and other electronic applications (Kahveci and Unal, 2000). However, in recent years, this technology has been extended to refining scraps; in Kahveci and Unal's study (Kahveci and Unal, 2000) a 5XXX series scrap material was tested. In the fractional crystallization process, the melt surface is cooled rapidly in order to form aluminum crystals. These purified crystals settle to the bottom of the furnace and the remaining liquid continues to accumulate impurities. The remaining liquid aluminum (containing high levels of impurities) is removed from the furnace first; this material is referred to as the "downgrade". The purified crystals left in the bottom of the furnace are then re-melted and removed; this material is referred to as the "upgrade". This process can be done in multiple refining steps to achieve a high purity metal.

This technology takes advantage of the thermodynamic behavior of dilute eutectic binary systems; specifically, above the eutectic temperature the solute material will be present in the liquid while the solid that forms will be high purity aluminum. One can estimate the degree to which an element can be removed by examining the binary phase diagram and calculating the thermodynamic or equilibrium distribution coefficient. In the literature, equilibrium distribution coefficients are calculated in two ways as either (1) the ratio of the solute concentration in the solid to the solute concentration in the liquid, or (2) the ratio of the solute concentration in the solid to the original concentration of the solute. The values as calculated according to Eq. (3) from two studies, one at Alcoa

Table 4

Equilibrium distribution coefficients as calculated by the Alcoa (Kahveci and Unal, 2000) and Delft (Sillekens et al., 2000) studies (×, not provided by Delft study).

	Alcoa	Delft
Sn	0.001	0*
Fe	0.03	0.03
B	0.045	×
Ni	0.008	0
Si	0.1	0.13
Cu	0.14	0.17
Ga	0.2	0.20*
Mg	0.25	0.45*
Zn	0.5	0.87*
Mn	0.93	0.62
Cr	1.9	×
V	2.4	×
Zr	2.55	×
Ti	6.7	×

* Estimated and not calculated for the Delft study.

Table 5

Boiling point of several metals.

Boiling point (°C)		Boiling point (°C)	
Zn	907	Al	2467
Mg	1107	Cu	2567
Pb	1740	Cr	2672
Mn	1962	Ni	2732
Si	2355	Fe	2750

(Kahveci and Unal, 2000) and one at Delft (Sillekens et al., 2000), are reported in Table 4. Elements that form a peritectic in the aluminum binary phase diagram will have equilibrium distribution coefficient greater than one (Cr, V, Zr, Ti) and will therefore accumulate in the upgraded portion of the melt. Therefore, these impurities must be removed from the melt before the refining process; this is typically accomplished using boride formation. The lower the distribution coefficient, the more that impurity will partition in the liquid and therefore more of it can be removed from the upgraded portion. For example, Fe, Ni, and Si can be almost wholly removed from the purified aluminum stream while Mn and Zn will remain in a higher concentration.

$$\text{Alcoa } k = \frac{C_{\text{solute in solid}}}{C_{\text{solute in liquid}}}, \quad \text{Delft } k = \frac{C_{\text{solute in solid}}}{C_{\text{solute original}}} \quad (3)$$

3.5. Distillation technologies

The increasing number of lithium containing aluminum alloys (typically 2% Li by weight) currently being produced has focused increased attention on methods to remove excess lithium in order to recycle these materials. Vacuum distillation has been identified as one of the few cost-effective techniques for removing lithium, which is very reactive to refractories in the melt phase (Rao, 2006). In most distillation processes, a metallic melt is held at a controlled temperature and vapor pressure. The melt is brought to above the boiling point of the element that is to be removed while remaining well below the boiling point of aluminum and most other metals present (Table 5). Vapor collection and condensation results in a high-purity byproduct in addition to the increased aluminum purity.

Zinc distillation is used to upgrade zinc containing metallic scrap streams in the zinc secondary processing industry. However, its extension to removing zinc from aluminum melts is still in the research and development stage. One study showed that a continuous agitation zinc distillation process was capable of reducing an aluminum melt with >3 wt.% zinc to less than 0.1 wt.% (Ohtaki

Table 6
Summary of upgrading technology capabilities and state of use in industry.

Technology		Ref.	Capability	Use
Physical separation and pre-melt technologies	Shredding	Rousseau and Melin (1989)	Size reduction of any scrap stream	Wide industry use ~200 facilities in North America
	Hand sorting	Spencer (2005)	Capabilities vary, separate non-ferrous components from each other at best	Industry use concentrated in low labor cost regions
	Magnetic sorting	Wilson et al. (1994)	Separate non-ferrous components from steel	Wide industry use
	Air separation	Veasey et al. (1993)	Separate lighter weight materials (foams, plastics, rubber, etc.) out of non-ferrous scrap stream	Wide industry use
	Heavy media/sink float	Rousseau and Melin (1989)	Separate non-ferrous components from each other (Al, Mg, Cu, etc.)	Industry use ~10 facilities in North America
	Eddy current	Kercher and Webb (1982), Schloemann (1982)	Separate metallic from non-metallic scraps	Wide industry use
	Color ID/etching	Wyss and Schultz (1999), Gesing et al. (2000), Schultz and Wyss (2000)	Separate zinc, copper, brass, and stainless steel from aluminum, in conjunction with etching can separate Al by alloy family	Some industry use
	Spectrographic techniques	Gesing et al. (2001b, 2003b), Gesing (2006)	Sort co-mingled streams by metal and alloy family, capability to sort by alloy in pilot plant stage	Small industry use, pilot plant scale
Chemical separation and melt technologies	Hoopes process/electrolytic	Kamavaram et al. (2003)	Removes Si, Fe, Mg, Mn, Cu, Zn, Cr	Industry use, small market
	Fractional crystallization	Kahveci and Unal (2000), Sillekens et al. (2000)	Removes Si, Fe, Mg, Mn,	Pilot plant scale, R&D
	Unidirectional solidification	Kondo et al. (1990)	Removes Si, Fe, Cu, Mg, Mn, Zn	Lab scale, R&D
	Distillation	Ohtaki et al. (2000)	Removes Zn, Li from Al melt	Pilot plant scale, R&D
	Hot crush	Ambrose et al. (1983), DeGaspari (1999)	Separate cast and wrought Al	Little industry use
	Filters	Frisvold et al. (1992), Oosumi et al. (2000)	Removes SiC, alumina inclusions	Wide industry use
	Flotation Fluxes	Veasey et al. (1993) Utigard et al. (1998)	Removes hydrogen Prevent oxidation; remove gases, Ca, Sr, Na, Mg, Li, inclusions from Al melt	Wide industry use Pervasive industry use

et al., 2000). The mass transfer coefficient, K , effectively the zinc removal rate, was calculated as:

$$K = \ln \left(\frac{C}{C_0} \right) \frac{V}{At} \quad (4)$$

where C is the zinc concentration, C_0 is the initial zinc concentration, A is the surface area of the melt, V is the volume of the melt, and t is the holding time. This removal rate was found to increase with an increase in holding temperature (Ohtaki et al., 2000). Distillation holds much promise for removal of impurity elements from aluminum as the removed element can be re-collected in a high purity state and therefore reused as well.

4. Inclusion and hydrogen removal

Impurities beyond tramp elements are also present in most recycled material streams. Inclusions, most commonly alumina, SiC, and intermetallic compounds, can be problematic in aluminum melts and must be removed to ensure certain properties. The removal of inclusions is typically done in one of three ways: (1) sedimentation, (2) flotation, and (3) filtration. Currently, alumina inclusions are also removed by injecting chlorine gas in the melt. However, due to the environmental and handling implications of this gas, studies (Beland et al., 1998; Roy et al., 1998) have successfully demonstrated using salt-flux injections, namely KF and NaF to replace chlorine gas use in inclusion removal. Their extension to replacing chlorine gas for other inclusion types (SiC, intermetallics) has been less successful (Utigard et al., 1998).

4.1. Sedimentation

Sedimentation is the process of letting higher density inclusion particles settle to the bottom of the furnace melt; this may require additional melt holding time and therefore energy and cost. This process would also apply to any metals that can be oxidized from the melt (mainly calcium and magnesium). The sedimentation process is governed by Stokes law and as such, the smaller the inclusions, the slower they will settle to the bottom of the furnace. Using the Navier–Stokes equations one can calculate a settling velocity, where the rate at which a particle will settle due to gravity is balanced by the frictional and buoyant forces:

$$V_s = \frac{2(\rho_{\text{particle}} - \rho_{\text{fluid}})gr^2}{9\mu} \quad (5)$$

where V_s is the settling velocity, ρ is the density, μ is the dynamic viscosity of the fluid, g is the gravity, and r is the radius of the particle assuming it is spherical. Engh found that for inclusion of a size typically found in aluminum melts (~100 μm alumina), the rates were far too slow (~8 cm/min) to be useful in most industrial applications.

4.2. Flotation

Also referred to as degassing, flotation is used to remove entrapped hydrogen from aluminum casting melts. Hydrogen is the only gas that has solubility in aluminum; this increases with melt temperature. It is the main cause of porosity in solidified

castings and ingots (Lin and Hoch, 1989). For the flotation process, a chlorine and argon gas mixture is injected in the bottom of the melt, as the bubbles rise, the hydrogen atoms diffuse to the bubble surface and produce hydrogen gas within, thus expanding the bubbles. When the bubble reaches the melt surface, the hydrogen gas is released. The bubbles also help to encourage other low density inclusions to migrate to the dross layer at the surface of the melt. The small percentage of chlorine in the gas will also help to remove alkali impurities as outlined in Section 3.1. The injection of fluxing agents combined with degassing or flotation technologies is the subject of a large body of research (Veasey et al., 1993).

4.3. Filtration

Filtration is the mechanical removal of unwanted particles and inclusions; the two most common types are cake and deep bed. In cake filtration, the liquid metal is passed through a small filter or screen; the particles and inclusions will be stopped and begin to accumulate, forming a cake. As this cake gets larger, its filtering capabilities increase. Studies have found that cake filtration is successful in removing inclusions larger than 0.03 cm (Frisvold et al., 1992). The more prevalent type of filtration in aluminum melting operations is deep bed filtration. A much larger filter with a more complex path of porosity is used in this case, increasing the path that particles and inclusions in the melt must travel. These particles then become entrapped in the filter through friction, confinement, electrostatic forces, and chemical bonding. Developing different filter materials is a large research area and successfully tested prototypes have been made from cordierite, fiberglass, steel, molybdenum, aluminum oxide, and silicon carbide bonded particles (Bakke et al., 1992; Desmoulin, 1992; Frisvold et al., 1992; Oosumi et al., 2000). The depth and porosity of the filters plays a large role in their inclusion removal efficiency (Keegam and McCollum, 1992).

5. Discussion and conclusions

Table 6 summarizes the technologies covered, their capabilities, and industry penetration. It should be noted that many more technologies not covered here are in the research and development phase. The uncertainty surrounding scaling up these technologies combined with the wide range in technologies already available highlights the fact that models are necessary in order for producers to properly choose which upgrading technology will have the most benefit in terms of value and increased scrap utilization for their specific inputs and production portfolio.

Creating models for exploring issues of mitigating compositional accumulation through upgrading technologies requires an understanding of (1) the flow of end-of-life scrap materials, (2) a method to evaluate how the economics of production are affected by changes in technology, and (3) a characterization of how recycling parameters influence accumulation in recycled streams. Each of these topics has been explored previously and each has a rich set of literature. Material flow analysis that tracks end-of-life aluminum scraps has been explored by the International Aluminum Institute (Boin and Bertram, 2005; IAI, 2005) as well as companies such as Alcoa (Bruggink, 2000; Martchek, 2000, 2006, 2007). Modelling tools for evaluating the economics of production are varied; many producers make use of linear optimization techniques (Lund et al., 1994). Blending problems have been addressed with linear programming models for decades (Metzger and Schwarzbek, 1961). These models can improve decisions about raw materials purchasing and mixing as well as the upgrading and sorting of secondary materials (Shih and Frey, 1995; Stuart and Lu, 2000; Cosquer and Kirchain, 2003). One body of work has looked at the useful

combination of dynamic material flow analysis combined with some form of batch planning optimization. This work has been implemented to address aluminum recycling policy questions on a large scale in Europe due in part to EU directives for automotive recycling. Studies by van Schaik et al. (2002), van Schaik and Reuter (2004) and Reuter et al. (2006) have used dynamic modeling and large datasets to calculate optimized recovery rates for end-of-life vehicles in order to guide operational and technological decisions by recyclers and to provide reasonable recovery expectations for recyclers, and more broadly, legislators. The authors have also applied dynamic material flow analysis with linear programming techniques to look at evaluating upgrading technologies on economic and environmental metrics (Gaustad et al., 2008) and market-motivated scrap allocation (Gaustad et al., 2011).

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References

- Alcoa. Alcoa 2020 strategic framework for sustainability. Available from http://www.alcoa.com/global/en/about.alcoa/sustainability/2020_Framework.asp; 2006.
- Ambrose F, Brown RD, Montagna D, Makar HV. Hot-crush technique for separation of cast- and wrought-aluminum alloy scrap. *Conservation & Recycling* 1983;6:63–9.
- Bakke P, Nordmark A, Bathen E, Engh TA, Oymo D. Filtration of magnesium by ceramic foam filters. Warrendale, PA: TMS: The Minerals, Metals, and Materials Society; 1992.
- Beland G, Dupuis C, Riverin G, Desmeules R, Rose L. Rotary flux injection: chlorine-free technique for furnace preparation. In: TMS: The minerals, metals, and materials society annual meeting; 1998.
- Boin UJM, Bertram M. Melting standardized aluminum scrap: a mass balance model for Europe. *Journal of Materials* 2005;57(8):26–33.
- Bruggink PR. Aluminum scrap supply and environmental impact model. In: Fourth international symposium on Recycling of Metals and Engineered Materials. TMS; 2000.
- Callister WD. Materials science and engineering: an introduction. New York, NY: John Wiley & Sons, Inc; 2000.
- Cosquer A, Kirchain R. Optimizing the reuse of light metals from end-of-life vehicles: lessons from closed loop simulations. TMS: The Minerals, Metals, and Materials Society; 2003, AA3 (Increasing Energy Efficiency in Aluminum): 73.
- Das SK. Emerging trends in aluminum recycling: reasons and responses. San Antonio, TX: TMS: The Minerals, Metals & Materials Society; 2006.
- DeGasperis J. Making the most of aluminum scrap. *Mechanical Engineering – CIME* 1999;121(11):71.
- Desmoulin J-P. Reliability of molten metal filtration. TMS: The Minerals, Metals, and Materials Society; 1992.
- Frisvold F, Engh TA, Johansen ST, Pedersen T. Removal of inclusions – a survey and comparison of principles. TMS: The Minerals, Metals, and Materials Society; 1992.
- Gaustad G, Olivetti E, Kirchain R. Economic and environmental evaluation of various aluminum scrap upgrading options using chance constrained optimization modeling. In: Global symposium on recycling, waste treatment, and clean technology (REWAS); 2008.
- Gaustad G, Olivetti E, Kirchain R. Design for recycling. *Journal of Industrial Ecology* 2010;14(2):286–308.
- Gaustad G, Olivetti E, Kirchain R. Toward sustainable material usage: evaluating the importance of market motivated agency in modeling material flows. *Environmental Science & Technology* 2011;45(9):4110–7.
- Gesing A. Recycling light metals from end-of-life vehicles. *Journal of Materials* 2001;53(11).
- Gesing A. Assuring the continued recycling of light metals in end-of-life vehicles: a global perspective. *Journal of Materials* 2004;56(8):18–27.
- Gesing A. ELVs: how they fit in the global materials recycling system and with technologies developed for production or recycling of other products and materials. In: International automobile recycling congress (IARC 2006); 2006.
- Gesing A, AuBuchon B, Torek P, Dalton R, Wolanski R. Assuring continued recyclability of automotive aluminum alloys: chemical-composition-based sorting of wrought and cast al shred. San Diego, CA: TMS; 2003a.
- Gesing A, Berry L, Dalton R, Wolanski R. Assuring continued recyclability of automotive aluminum alloys: grouping of wrought alloys by color, X-ray absorption and chemical composition based sorting. Seattle, WA: TMS; 2002.
- Gesing A, Harbeck H. Particle sorting of light-metal alloys and expanded use of manufacturing scrap in automotive, marine, and aerospace markets. In: Global

- symposium on recycling, waste treatment, and clean technology (REWAS); 2008.
- Gesing A, Stewart C, Hopson G, Costello S, Lambert S, Good T, et al. Separation of wrought fraction of aluminum recovered from automobile shredder scrap. New Orleans, LA: TMS; 2001a.
- Gesing A, Stewart C, Hopson G, Costello S, Lambert S, Good T, et al. Separation of wrought fraction of aluminum recovered from automobile shredder scrap. The Minerals, Metals & Materials Society; 2001b.
- Gesing A, Stewart C, Wolanski R, Dalton R, Berry L. Scrap preparation for aluminum alloy sorting. In: Fourth international symposium on recycling of metals and engineering materials; 2000.
- Gesing A, Torek P, Dalton R, Wolanski R. Assuring recyclability of automotive magnesium alloys: chemical composition-based sorting of magnesium shredded scrap. San Diego, CA: TMS; 2003b.
- Green JAS. Aluminum recycling and processing for energy conservation and sustainability. Materials Park, OH: ASM International; 2007.
- IAI. Sustainability update 2005. Aluminum for future generations. London, UK: International Aluminium Institute; 2005.
- Kahveci AI, Unal A. Refining of a 5XXX series aluminum alloy scrap by alcoa fractional crystallization process. In: Fourth international symposium on recycling of metals and engineered materials. TMS: The Minerals, Metals, and Materials Society; 2000.
- Kamavaram V, Mantha D, Reddy RG. Electrorefining of aluminum alloy in ionic liquids at low temperatures. *Journal of Mining and Metallurgy* 2003;39(1–2):43–58.
- Keegam NJ, McCollum JM. Depth of ceramic foam filter vs. filtration efficiency. TMS: The Minerals, Metals, and Materials Society; 1992.
- Kelly TD, Matos GR. Historical statistics for mineral and material commodities in the United States. Aluminum. Retrieved 7-12-10, 2010, from <http://pubs.usgs.gov/ds/2005/140/>; 2010.
- Kercher SA, Webb M. Scrap processing by eddy current separation techniques. *Resources and Conservation* 1982;8:61–74.
- Kim J-Y, Kim S-J, Song I-K, Han J-H. Aging characteristics of recycled ACSR wires for distribution lines. In: Electrical insulation conference and electrical manufacturing & coil winding conference; 1997.
- Kondo M, Maeda H, Mizuguchi M. The production of high-purity aluminum in Japan. *Journal of the Minerals, Metals, and Materials Society* 1990;42(11):36–7.
- Krotkov M, Satayev I, Shepelev D. Technology and equipment for X-ray radiometric sorting of secondary metallic raw materials. In: XVIII international mineral processing congress; 1993.
- Kubaschewski O, Evans ELL, Alcock CB. Metallurgical thermochemistry. Oxford: Pergamon; 1979.
- Lin RY, Hoch M. The solubility of hydrogen in molten aluminum alloys. *Metallurgical Transactions A* 1989;20A(September):1785–90.
- Liu Z-K. Effect of impurities on alloys. I. T. Program. Washington, DC: Energy Efficiency and Renewable Energy, US Department of Energy; 2003.
- Lund JR, Tchobanoglous G, Anex RP, Lawver RA. Linear programming for analysis of material recovery facilities. *Journal of Environmental Engineering* 1994;120(5):1082–94.
- Lundqvist U, Andersson B, Axsater M, Forsberg P, Heikkilä K, Jonson U, et al. Design for recycling in the transport sector – future scenarios and challenges. Goteborg, Sweden: Chalmers University of Technology, Goteborg University; 2004.
- Martchek KJ. The importance of recycling to the environmental profile of metal products. *Recycling of Metals and Engineered Materials*, TMS; 2000.
- Martchek KJ. Modelling more sustainable aluminium. *International Journal of Life Cycle Assessment* 2006;11(1):34–7.
- Martchek KJ. Material flow modeling of aluminum for sustainability. In: Green JAS, editor. Aluminum recycling and processing for energy conservation and sustainability. Materials Park, OH: ASM International; 2007. pp. 103–107.
- Metzger RW, Schwarzbek R. A linear programming application to cupola charging. *The Journal of Industrial Engineering* 1961;12(2):87–93.
- Minter A. Where America recycles. Washington, DC: The Atlantic; 2006.
- Ohtaki M, Arakawa T, Murata F. A new proposal of continuous agitation vacuum distillation process (CAVP) to remove Zn from aluminum scrap melt. In: Fourth international symposium on recycling of metals and engineered materials. TMS: The Minerals, Metals, and Materials Society; 2000.
- Oosumi K, Nagakura Y, Masuda R, Watanabe Y, Ohzono T. Development of new filter for removal of non-metallic inclusions from the molten aluminum. In: Fourth international symposium on recycling of metals and engineered materials at the TMS fall extractive process metallurgy meeting. The Minerals, Metals & Materials Society; 2000.
- Plunkert P. Aluminum. US Geological Survey Minerals Yearbook. USGS; 2010.
- Ragone DV. Thermodynamics of materials. New York: John Wiley & Sons, Inc; 1995.
- Rao SR. Resource recovery and recycling from metallurgical wastes. Oxford, UK: Elsevier; 2006.
- Reuter MA, van Schaik A, Ignatenko O, de Haan GJ. Fundamental limits for the recycling of end-of-life vehicles. *Minerals Engineering* 2006;19:433–49.
- Rousseau M, Melin A. The processing of non-magnetic fractions from shredded automobile scrap: a review. *Resources Conservation and Recycling* 1989;2:139–59.
- Roy R, Utigard TA, Dupuis C. Inclusion removal during chlorine fluxing of aluminum alloys. Warrendale, PA: TMS: The Minerals, Metals, and Materials Society Annual Meeting; 1998.
- Sattler H. Automatic sorting of non-ferrous metals from automobile shredders. TMS: The Minerals, Metals, and Materials Society; 1990.
- Sattler H, Yoshida T. New sorting system for recycling of magnesium and its alloy after use. In: First international conference on process materials for properties; 1993.
- Schloemann E. Eddy-current techniques for segregating of NF-metals from waste. *Conservation & Recycling* 1982;5(2/3):149–62.
- Schultz P, Wyss R. Color sorting aluminum alloys for recycling – Part II. Plating and Surface Finishing 2000;87(6):62–5.
- Shih JS, Frey HC. Coal blending optimization under uncertainty. *European Journal of Operational Research* 1995;83:452–65.
- Sillekens WH, Schade Van Westrum JAFM, Bruinsma OSL, Behmetaj B, Nienoord M. Refining aluminum scrap by means of fractional crystallisation: basic experimental investigations. In: Fourth international symposium on recycling of metals and engineered materials. TMS: The Minerals, Metals, & Materials Society; 2000.
- Spencer DB. The high-speed identification and sorting of nonferrous scrap. *Journal of Materials* 2005;57(4):46–52.
- Stuart JA, Lu Q. A model for discrete processing decisions for bulk recycling of electronics equipment. *IEEE Transactions on Electronics Packaging Manufacturing* 2000;23(4):314–20.
- Utigard TA, Friesen K, Roy R, Lim J, Silny A, Dupuis C. The properties and uses of fluxes in molten aluminum processing. *Journal of Materials* 1998;November:38–43.
- van Schaik A, Reuter MA. The time-varying factors influencing the recycling rate of products. *Resources Conservation & Recycling* 2004;40:301–28.
- van Schaik A, Reuter MA, Boin UMJ, Dalmijn WL. Dynamic modelling and optimisation of the resource cycle of passenger vehicles. *Minerals Engineering* 2002;15:1001–16.
- Veasey TJ, Wilson RJ, Squires DM. The physical separation and recovery of metals from wastes. Amsterdam: Gordon and Beach Science Publishers; 1993.
- Viklund-White C, Menad N. Impurity accumulation as a consequence of increased scrap recycling. Stockholm, Sweden: Minerals and Metals Recycling Research Centre, MiMeR Lulea University of Technology; 1999, 35 p.
- Wilson RJ, Veasey TJ, Squires DM. The application of mineral processing techniques for the recovery of metal from post-consumer wastes. *Minerals Engineering* 1994;7:975–84.
- Wyss R, Schultz P. Color sorting aluminum alloy scrap for recycling. *Light Metals* 1999.