5-14-2015

Exploring Property based Aluminum Specifications.

Naitik Gada

Exploring Property based Aluminum Specifications.

By

Naitik Gada

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science and Engineering

School of Chemistry and Material Science

College of Science

Rochester Institute of Technology

Rochester, NY

May 14th, 2015.

Committee Approval:

Dr. Gabrielle Gaustad **Date**

Associate Professor in Golisano Institute for Sustainability, Faculty Member for School of Materials Science and Engineering and Thesis Advisor.

Dr. Seth Hubbard **Date**

Associate Professor in College of Science and Committee Member.

Dr. KSV Santhanam **Date**

Professor in School of Chemistry and Materials Science and Academic Advisor.

ABSTRACT

Aluminum recycling is imperative because of the steady increase in its consumption. Recycling creates a secondary supply stream, lowers production costs and significantly reduces energy use during the production cycle. One of the limiting factors to increased use of scrap in alloys is problematic tramp elements that accumulate in the scrap stream. Currently, alloy producers make use of blending models to assist in choosing from a large number of inputs (scrap sources, primary aluminum, and alloying elements) to manufacture a portfolio of alloys within specification. The goal is to present cost-effective strategies to increase scrap consumption under the applicable context of different operating environments in aluminum production. These blending tools also aim to foster a fundamental shift in decision-making behavior to factor in uncertainties into the scrap management process. Alloys are batched to specification to maximize alloy function which includes a complex set of desired properties. While AA specifications have been put in place to guide batch blending decisions, often maximum constraints result in conservative scrap utilization, thus minimizing the potential for environmental and economic savings. With the wide variety of aluminum alloys available, batching them with the right applications is of the utmost importance, which becomes easier with property based constraints. While the blending models batch the alloys according to the specifications, it is equally necessary to batch them based on their properties to ease the decision making in the scrap management. This trade-off was presented using a linear programming optimization model that tracked four main alloying elements – silicon, magnesium, iron and copper. The optimization model examined the problem of mixing arbitrary quantities of raw materials (scrap aluminum, pure allowing elements and pure aluminum) to produce a set of alloys that met the property based specifications.

For this thesis work, a few selected properties - electrical resistivity, density, elastic modulus and the melting point of aluminum were used as constraints to drive increased scrap use without negatively affecting the performance of the alloys. Results show that increased scrap utilization is possible for a set of specific cases.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor, Dr. Gabrielle Gaustad for the opportunity and honor to work and conduct research under her. Her help, advice and guidance are the reasons I was able to view the light at the end of the tunnel. Her intellect and presence during the time I was working on my thesis was a constant reminder for me to strive to be better, as a person and as a student. Through all the ups and downs, the delays and struggles to be able to finish this thesis, her constant support and encouragement were nothing short of a blessing. Coming out on the other side, I can say that I wouldn't have had it any other way. You make me want to be a better student every day. My respect for you has only increased through all this time. With all my sincerity, I thank you for one of the most grueling and best experiences of my career.

Secondly, I want to thank my dearest and my closest friend, Osborn de Lima. You have been there from day 1 and without your presence in my life, this day would not have been possible. From crashing on your couch, endless conversations to mooching off of you for basically a year, your support is why I believe in miracles. I look up to you in ways that cannot be counted and will continue to keep doing so. Thank you, my friend. I'm truly grateful that you're in my life.

Lastly, I want to thank my parents – Hemant and Hansa Shah who are the pillars on which I have built my life. You are the light that guides me through the darkest of times and the strength that keeps me moving. You are who I worship. Without your love and affection, your sacrifices and hardships, your encouragement and motivation, I would not have lived to see this day. All I am today is because of you; my deepest and most sincere gratitude.

TABLE OF CONTENTS

1. Introduction

1.1 Material consumption in the world

Global material consumption today is at its highest with the growing population of the world. As this population continues to grow, the rate of consumption of materials is also going to increase. Figure 1 shows the material consumption per capita per person in different parts of the world. As illustrated, a full ruck sack amounts to 20 kilograms of material consumed per person per day. North America consumes the highest with about 102 kilograms of material used per capita per day, whereas in Africa only 11 kilograms of material are consumed daily per person. On a global level, material consumption equates to resource extraction: the world economy uses around 68 billion tons of resources each year to produce the goods and services; which we all consume (SERI, 2004).

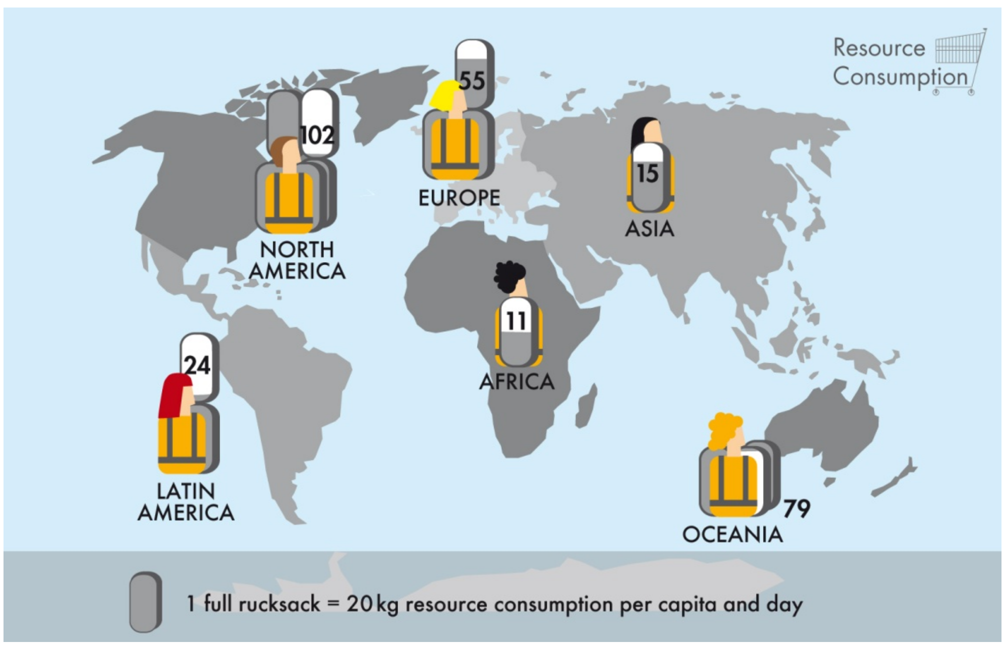

Figure 1: Global resources consumption per capita per day (SERI, 2004).

Materials derived from natural resources are classified as renewable or non-renewable. When the rate of consumption of materials exceeds the supply of these resources, prices go up and the scarcity may lead to a global crisis. An increase in material consumption of emerging and developing countries to ensure at least a minimum level of quality of life would require a decrease in resource use of industrialized countries in order to be sustainable. It is evident from Figure 1 that developing countries like the ones in Africa, Asia and Latin America use significantly less resources compared to the developed countries of Europe and North America. Some non-renewable resources are formed over a long period of time and are limited in supply. Therefore, the amount of natural resources that mankind can use without harming the ecosystem is also limited. Figure 2 shows the trend of material consumption through the years in the United States. It is evident that the consumption has constantly been on the rise. A simple extrapolation of this data into the future is enough to further portray this trending rise in consumption. Industrial minerals account for the top spot in the consumption profile followed by metals (both primary and recycled). Agricultural and other renewable resources are consumed less as compared to the non-renewable resources, an irony considering there is a limit to the supply of many non-renewables.

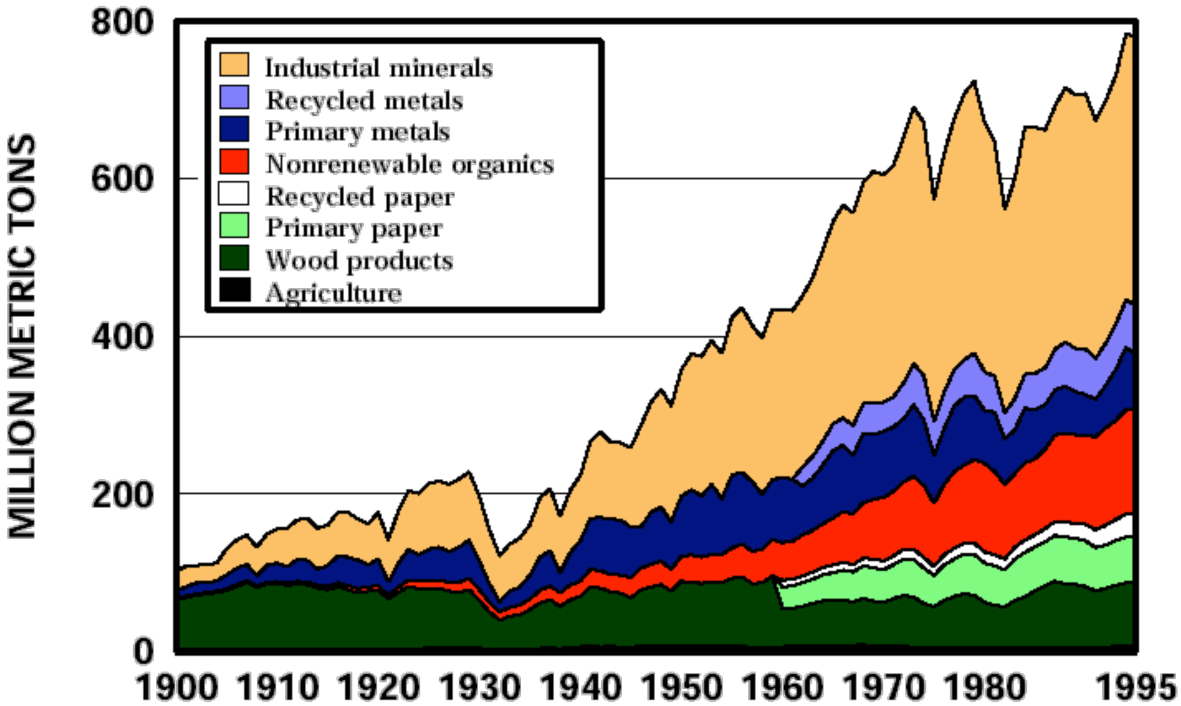

Figure 2: Trend in the material consumption in the 20th century (Matos and Wagner, 1998).

1.2 Impacts of material use

Material consumption at such a high rate has consequences on our environment. Potential impacts include climatic changes, harmful emissions into the environment, the depletion of our precious natural resources, constant increase in the global energy consumption. A side-effect of such a high rate of material use is the increased energy consumption. The energy that is consumed in the production of some of these materials is quite high. Table 1 gives some numerical values to support this claim; light metals like titanium and aluminum are the highest energy consumers for their production cycle consuming 361 MJ/kg and 211 MJ/kg of energy respectively (cradle to gate), followed by nickel that consumes 114MJ/kg by the flash furnace smelting and 194 MJ/kg by the pressure acid leaking processes. Steel and lead (by the blast furnace process) have the lowest cradle to gate environmental impacts in terms of the gross energy required to produce one kilogram of the metal – 23 MJ/kg and 20 MJ/kg respectively. Fossil fuels are limited and mankind should start contemplating on the long-term effects of such a large magnitude of energy consumption. One source confirms that about 7% of the world's energy use goes into the metal sector (Norgate et. al., 2006). The physical properties of ores from mining are first improved and then the ore is chemically transformed to extract metals and produce industrial materials. This requires significant amounts of energy. Life Cycle Assessment (LCA) methodology involves the compilation of an inventory of relevant environmental exchanges during the life cycle of a product and evaluating the potential environmental impacts associated with those exchanges. The full product life cycle is usually divided into the following stages (Norgate et al. 2006): cradle to entry gate (raw material extraction and refining); entry gate to exit gate (product manufacture); and exit gate-to-grave (product use, recycling and disposal). One form of energy use included in LCAs is the Gross Energy Requirement (GER), also referred to as embodied energy or cumulative energy demand, which is the cumulative amount of primary energy consumed in all stages of a metal's life cycle (Norgate et al. 2006).

Metal	**Process**	**GER (MJ/kg)**	**GWP (kg CO2/kg)**
Nickel	Flash furnace smelting and Sherritt-Gordon refining.	114	11.4
	Pressure acid leaching	194	16.1
Copper	Smelting/Converting and Electro-refining	33	3.3
	Heap Leaching	64	6.2
Lead	Lead blast furnace	20	2.1
	Imperial smelting process	32	3.2
Zinc	Electrolytic process	48	4.6
	Imperial smelting process	36	3.3
Aluminum	Bayer refining, Hall-Heroult smelting	211	22.4
Titanium	Becher and Kroll processes	361	35.7
Steel	Integrated Route	23	2.3
Stainless Steel	Electric furnace and Argon-Oxygen decarburization	75	6.8

Table 1: Environmental Impacts for cradle-to-gate metal production (Norgate et al., 2006).

The energy source used to generate the electricity consumed in a particular metal production process also influences the ''cradle-to-gate'' environmental impact of that process. This may be illustrated by considering primary aluminum production (Norgate et al., 2006). The three main energy sources used for generating electrical power for aluminum production worldwide in 2003 were coal 36%, hydroelectricity 49% and natural gas 9%. The effect of these three electricity energy sources on the GER and GWP for primary aluminum production is shown in Fig. 3 (Norgate et al., 2006).

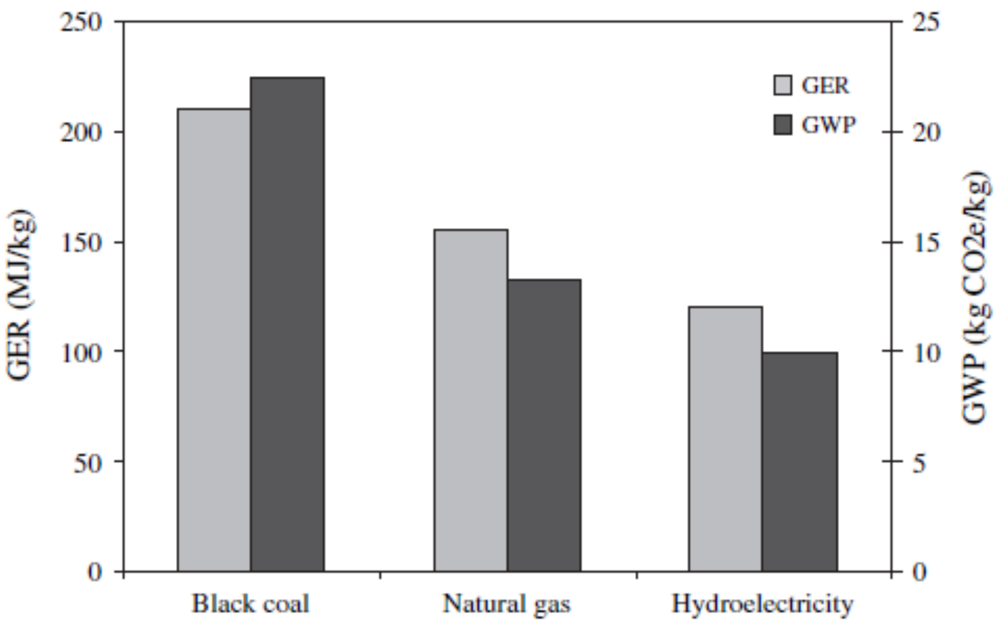

Figure 3: GER and GWP contribution of electricity sources for primary aluminum production (Norgate et al. 2006).

Apart from constant energy consumption, the global material use also brings with it depletion and degradation of the natural resources as stated before. This depletion in natural resources potentially affects our global climate and has negative impacts on the environment. The biocapacity of any given area is its ability to produce or provide resources and take in the waste. According to one source (Schaefer et. al., 2006), biocapacity is the measure of how sustainable a resource is, with regard to the ecological footprint. Ecological footprint measures the human demand for resources. When the ecological footprint of an area overshadows its biocapacity, consequences of an unsustainable nature occur. This means that the resources are more in demand than their supply and are under the risk of running out. Natural resources that are non-renewable can only be restored at regular intervals of time; some of these resources like fossil fuels that are one of the top sources of electricity are restored over thousands of years. With such long duration of a resource turn around, it is important that they be used very wisely. The Earth's regenerative ability cannot match the pace at which the resources are currently being used. To put it in numbers, a report generated by the US Environmental Protection Agency calculated that 'in 2005, the global biocapacity was measured as 2.1 hectares per capita, while the average demand or footprint per person was about 2.7 hectares'. In addition, whatever natural resources are being used cannot be retrieved immediately and are generally returned back as pure waste (USEPA, 2009). The growing demand of the resources and the shortage of supply are in turn causing a rise in commodity prices.

An added consequence of the material use and the apparent energy consumption is the global climatic changes. The increasing ecological footprint is a large factor that shapes the global climate. As shown in Figure 3, black coal is the main source of energy for the primary aluminum production. Burning black coal to generate electricity is a very popular option. Burning coal releases carbon particles into the atmosphere, increasing our carbon footprint. The carbon molecules in the air trap the heat from the sun and keep it within the atmosphere causing global warming. There are also non carbon molecules like nitrous oxide, ozone, etc. that trap the heat within earth's atmosphere. The resulting warm air around us has shaped our climate to a great extent. The leaders attending the Energy Summit of the United Nations in 1992 clearly stated that "a principal cause of the continued deterioration of the global environment is the steady increase in materials production, consumption and disposal" (United Nations, 1992). According to one source, humans have consumed more resources in the past 50 years than they have consumed all throughout history (IPSM, 2008). Also, between 1970 and 1995, the worldwide consumption of raw materials doubled (USGS, June 2008). Such high rate of consumption to match the high rate of population growth has side-effects. USEPA states that due to this magnitude of consumption of material resources, half of the world's tropical and temperate forests are now gone, freshwater withdrawals doubled since 1960 and due to the ever growing temperatures in the dry seasons; major rivers like Nile, Ganges, Mississippi sometimes do not reach the ocean completely (USEPA, 2009). For metals, it is the mining and refinery stage that is often very energy intensive, causing fossil-fuel-related emissions. In the case of intensive agricultural processes, growing can also be very polluting. Metals are elements and therefore not degradable; once in the environment, they do not disappear, but accumulate in soils and sediments. Different metals contribute to environmental toxicity in different amounts as is portrayed in Figure 4 (UNEP, 2010).

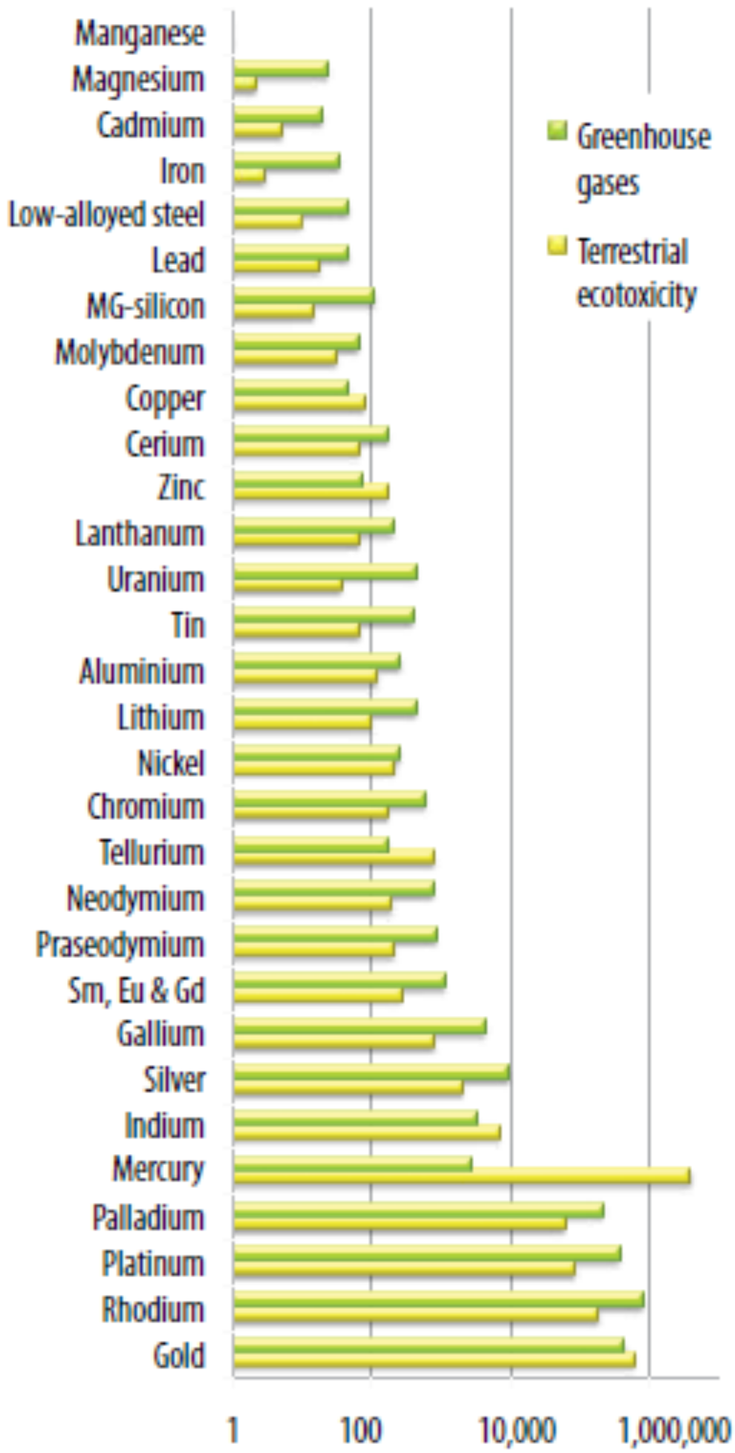

Figure 4: Contribution to terrestrial eco-system toxicity and global warming of 1kg primary metal (UNEP, 2010).

1.3 Recycling

For the factors stated above it is imperative that metals are recycled at a much larger scale. Apart from the obvious economical advantage, the energy savings also create a strong incentive to recycle. One of the most significant factors in the life cycle of a metal product is that recycling has the potential to reduce production energy dramatically. Some examples include the reduction in materials production energy consumption by 95% for aluminum, 80% for magnesium and lead, 75% for zinc, and 70% for copper (Martchek, 2000). A report by the U.S. Department of Energy states that "aluminum production is the largest consumer of energy on a per-weight basis and is the largest electric energy consumer of all manufactured products" (USDOE, 2007). Numerically, the aluminum industry in the United States consumes about 45.7 x 10^9 kilowatt hours of electricity which equates to more electricity than the amount consumed by the residential, industrial and commercial sectors of the U.S. economy together (USDOE, 2007). It further states the difference between the theoretical primary aluminum production energy required and the actual energy used. On an average the minimum theoretical energy required for the production of aluminum in the US is about 36 x 10^9 kilowatt hours of energy. The actual amount of energy consumed in the US is about 90 x 10^9 kilowatt hours (USDOE, 2007). It is clear that more energy is being used than necessary by industrial processes like smelting, which uses about 46% percent of the total energy consumed in the US. Smelting is the largest consumer of energy for aluminum manufacturing and is also the most technically complex. Process heating, which is utilized in almost all aluminum production operations amounts to about 27% of the total energy in the US (USDOE, 2007). Industrial processes like these that consume energy at significantly higher rates than the theoretical requirements need improvement (USDOE, 2007).

The practice of recovering metals for their value dates back to ancient times (Wilson, 1994) and today, the protection of earth's resource endowments and ecosystems adds to the incentive of recycling metals after their use. Global material consumption trends together with the unavoidable population growth lead to an increase in the consumption of natural resources. The inefficient use of metals and their improper disposal creates an unnecessary burden on the non-renewable resources of the earth from which they are extracted. The dumping of used metal has harmful effects on the environment. Some of these pollutant metals are non-degradable and their presence in the ecosystem may jeopardize the health of all living beings (Nriagu, 1988). One way to reduce such an atrocity to our precious ecosystem is to recycle on a vast scale. If the sustainable use of material resources is to be achieved, a secondary production industry is very important to be brought into the picture. In the last decade or so, secondary production of aluminum has been quite stale as the recycling rates remain below 50% (Gaustad et. al., 2007). One source guesses the reason for this modest increase to be the accumulation of the secondary production of the material over time (Ayres et. al, 2000). Furthermore, metals are eminently and repeatedly recyclable, while maintaining all their properties. Properties of a material play a crucial role in the life of a material; in the sense that the functionality of any given material is decided based on its properties. Their durability relative to many hydrocarbon based materials enhances their life cycle performance. However, the persistence of metals when dispersed into our natural environmental makes recovery and recycling particularly important. When considering life cycle effects, recycling is critical to a sustainable future for metal products (Martchek, 2000). Iron tops the list at about 517 MMT (million metric tons) followed by aluminum which is about 20 MMT (Ayres, 1997). Although a significant amount of aluminum is produced compared to the other metals, a secondary production industry of aluminum is very crucial. The current industry does not operate at the numbers that are necessary for a long term sustainable use of aluminum. As stated before, the recycling rates are below 50% (Gaustad et. al., 2007). Further studies have shown that out of the amount of aluminum that is recycled, 35% consists of the end-of-life materials (Gaustad et. al., 2010). These end-of-life materials or "old scrap" are materials that have either been discarded or have been outdated post-consumer use. The old scrap normally comes from automotive parts, construction materials, used beverage cans etc. and is comparatively harder to recycle than the new counterparts because of the vast mixture of the different kinds of alloys in the scrap. The challenge arises mainly because the metal that is to be recycled is mixed with various other materials and the contamination from these different materials leads to unnecessary buildup of unwanted scrap in the stream. This further jeopardizes the recycling of the metal of interest (Kim et. al, 1997 and Hatayama et. al. 2007). Recycling barriers like the ones mentioned in the previous statements can be overcome. According to the findings by Gaustad et. al., recycling barriers can be overcome by using strategies like "1. Changing the form and composition of the returning scrap, 2. Changing the characteristics of the process that converts scrap to finished goods and 3. Changing the specifications by which a finished good is judged acceptable" (Gaustad et. al., 2010).

1.4 Case Study: Aluminum

It is not uncommon to know that aluminum, the youngest industrial metal is also one of the most sought after materials. Due to its properties like ductility, malleability, conductivity and its toughness, it matches up to iron and yet is almost 3 times as light (Boin and Bertam, 2005). It is well known that the oxide of aluminum cannot be reduced to pure aluminum metal using either carbon or hydrogen, that is, in a water medium. This is because aluminum is highly reactive with the protons of water, which leads to the formation of hydrogen. The primary production of aluminum must, thus use an electrolysis process to produce pure aluminum metal from its oxide alumina (Al_2O_3) (Boin and Bertram, 2005). Charles Hall was the first person who successfully produced aluminum through electrolysis. He started by electrolyzing aluminum salts in water. His first attempts were unsuccessful because of the reaction of aluminum with the protons of water, leading to the formation of hydrogen. This led him to research on a variety of other salts that could serve the purpose of producing aluminum. When he finally passed a current through a solution of alumina dissolved in cryolite, small traces of aluminum were found in the electrolyzed solution. This process was adopted and has since been modified. It is now called the Hall-Heroult process and is the most-widely used method of producing aluminum through electrolysis (Alcoa, 1999).

Primary aluminum production starts by first converting bauxite to alumina. Bauxite is first crushed to get uniformly sized particles that are then mixed with a sodium hydroxide solution at high temperature and pressure in large grinding mills.

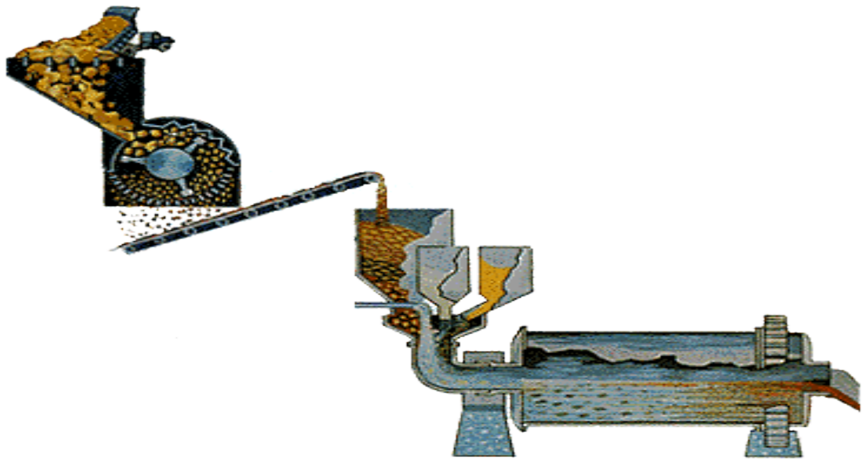

Figure 5: Crushing and grinding of the ore in the Bayer process (Alcoa, 1999).

This process discharges slurry, which is even finer in consistency and is pumped into a digester where the chemical reaction to dissolve alumina takes place. The sodium hydroxide solution is added as necessary to extract more alumina from the slurry and the resulting solution is then transferred into settling tanks.

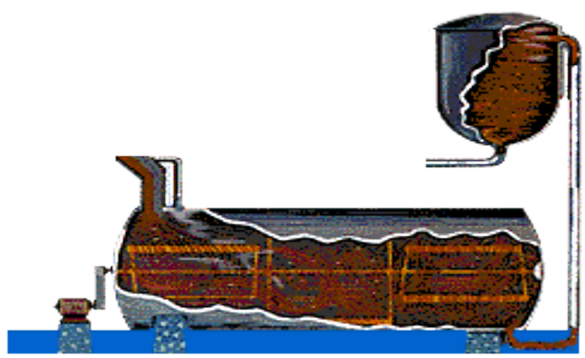

Figure 6: Digesting of the sodium aluminate solution (Alcoa, 1999).

Gravity is the main driving factor in achieving settling. The unwanted matter settles at the bottom of the tanks while the liquid at the top is filtered. It is then washed to recover the dissolved alumina and caustic soda. The remaining "slurry" is dried by evaporation. In the filter, the material that is caught is known as a filter cake; it contains alumina and caustic soda. The filtered liquor, a sodium aluminate solution is cooled and pumped to the precipitators.

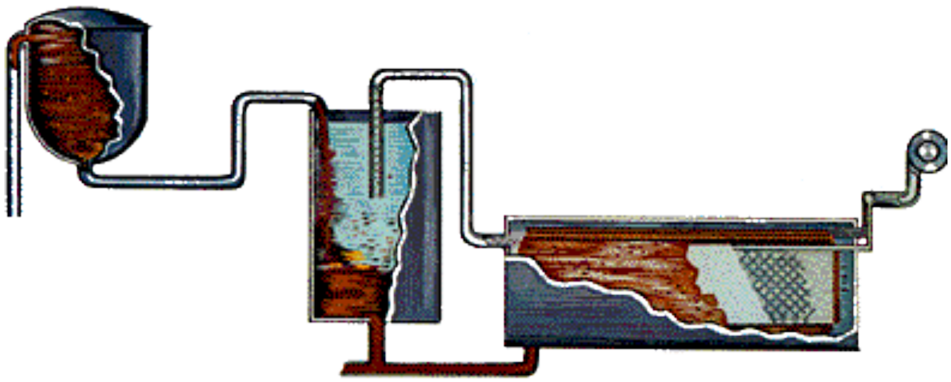

Figure 7: Settling of the mixture (Alcoa, 1999).

The large tanks known as precipitators are used for the precipitation of the pure alumina particles. The clear sodium aluminate solution from the settling is pumped into these precipitators with fine particles of alumina (seed crystals) to help with the precipitation process. When the crystals form around these seeds, they settle to the bottom of the tank. They are then removed and filtered twice before being transferred to the calcinations kilns.

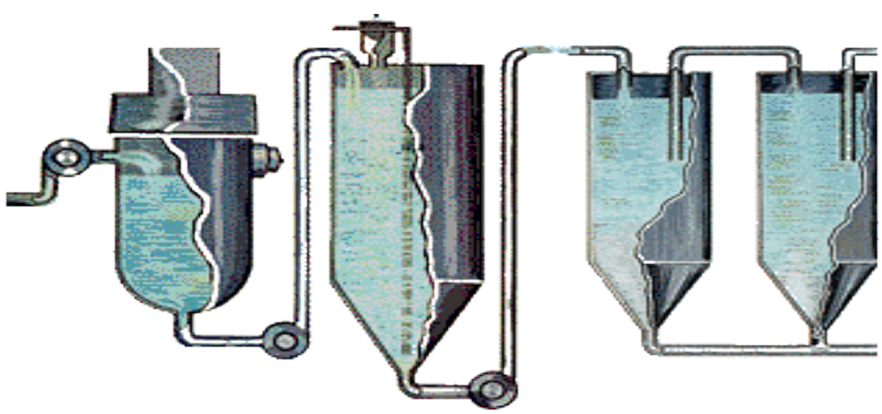

Figure 8: Precipitation of alumina particles (Alcoa, 1999).

Calcination is done to remove the water from the aluminum hydrate which is then referred to as the anhydrous alumina. The crystals from the precipitation that sink to the bottom of the tanks are moved on to the conveyer system that passes through the kilns. These kilns are brick lined inside and heated up to a temperature of about 1100^{o}C. The rotating kilns help in drying out the alumina evenly. The result is a fine white powder which is referred to as pure alumina (Alcoa, Reynolds Aluminum, Aluminum Institute).

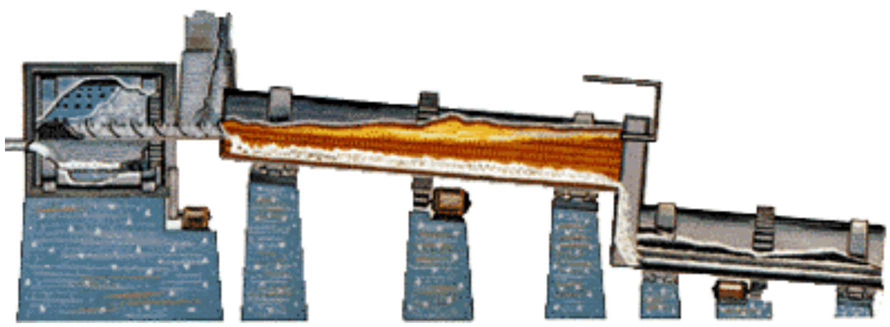

Figure 9: Calcination of the alumina hydrate (Alcoa, 1999).

Stage 2 of creating aluminum from bauxite is to convert the pure alumina to metallic aluminum. This is achieved by an electrolysis process called the Hall-Heroult process. As mentioned above, the Hall-Heroult process was put into practice in 1886 by Charles Hall, an American student and Paul Heroult, a French scientist. Both made the same discovery – that cryolite could be used to convert pure alumina into metallic aluminum. It takes place in a carbon or graphite lined steel container. An electrical current is passed through the cryolite mixture that contains pure alumina. This electric current, which is actually a direct current (DC) is necessary for the transformation from pure alumina to metallic aluminum. Although the voltage for this process is extremely low (about 5.2V), the amperage is generally very high, in the range of 100,000 – 150,000 amperes or more. The setup contains a carbon anode, positively charged made of petroleum coke and pitch and a cathode, negatively charged that is formed by the carbon or the graphite lining of the pot. When the electric current flows from the anode to the cathode, the carbon of the anode blends with the oxygen from the alumina. This reaction produces carbon dioxide as the by product and molten, metallic aluminum settles down at the bottom and is then drawn out periodically into crucibles, while the carbon dioxide escapes. A very little amount of cryolite is lost in the process and the alumina keeps getting replenished from the containers above the pots. The metallic aluminum collected at the bottom is now ready to be forged, turned into alloys, or is shaped to make everyday goods like appliances, automobiles, cans, etc.

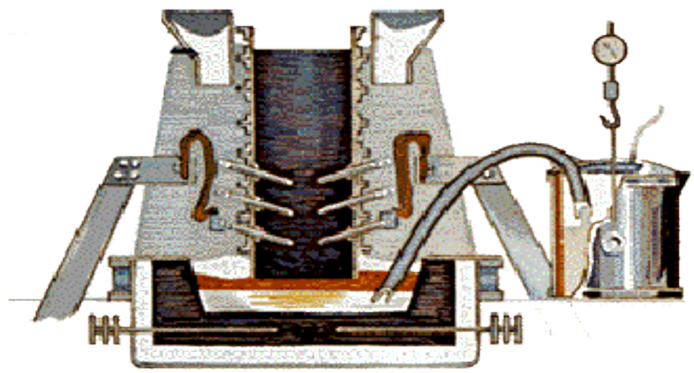

Figure 10: Electrolysis of aluminum by the Hall-Heroult process (Alcoa, 1999).

Commercially, the Hall-Heroult process is the most widely used process for primary aluminum production. The earlier stages of the primary aluminum production are called the Bayer process and the smelting part is known as the Hall-Heroult process (Norgate et. all, 2006). It is the electrolysis that makes this production process one of the most energy burden-intensive processes for materials, only second after the Becher and Kroll processes to produce titanium. This has clearly been shown earlier in Table 1 that gives the numbers for the amount of energy that is utilized by the production processes for various materials. As mentioned earlier, the Hall-Heroult process involves electrolysis or the smelting of alumina. Various aluminum production companies are spread across the United States where the conditions are favorable – availability of skilled labor, the proximity to a consumer market and provisions for a highly developed infrastructure. The United States Department of Energy wrote a report on the requirements for aluminum production in which it claimed that hydroelectric power accounts for 50% of the energy used worldwide for the electrolysis of aluminum. A major portion of the energy used in the production of aluminum is related to the electricity required for the electrolysis process, i.e. the Hall-Heroult process. Due to reasons like above, the production plants are now shifting base to the areas with low costing electricity. The figure below shows the tacit energy consumption of the major processes in the aluminum production chain. Production of the primary aluminum accounts for 87% of the energy consumed by the industry in the United States (USDOE, 2007). Production of the secondary aluminum accounts for 4.3%, rolling makes up 3.3%, extrusion accounts for 1.5% and finally, shape casting for the remaining 3.4 % (USDOE, 2007).

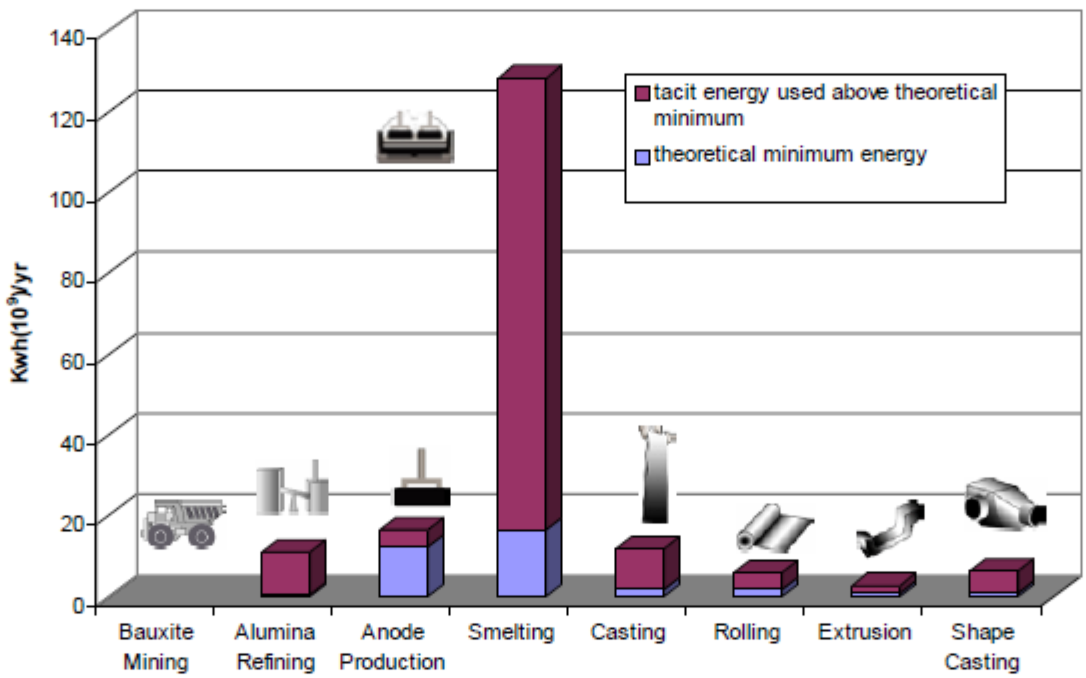

Figure 11: Comparison of the energy consumption between the various aluminum production processes in the United States (USDOE, 2007).

It's the industrial processes like these that make the recycling of aluminum and the increase in the production of secondary aluminum an absolute necessity. The environmental impacts of primary production are gargantuan and contribute to the Global Warming Potential of a particular material. The production of metals directly and indirectly, leads to the formation of emissions like unwanted by-products, harmful and toxic gases, unwanted solids etc. This mainly happens during processes like mining, the consumption of raw materials and electric power, manufacturing of reagents. In the case of aluminum, it's the waste created during the Bayer process and the chemical discharge during the electrolysis that is harmful to the environment. Figures given below compare the Gross Energy Requirements and the Global Warming Potential of various materials. It is not surprising to notice that aluminum is the second highest consumer of energy for its production, after titanium. Similarly, it stands second to titanium on the Global Warming Potential scale as well. Both these charts are alarming and are proof enough to incentivize the recycling of aluminum on vast scales. Programs that improve the thermal and electrical efficiency of the production processes, while minimizing the harmful by-products are to be sought after.

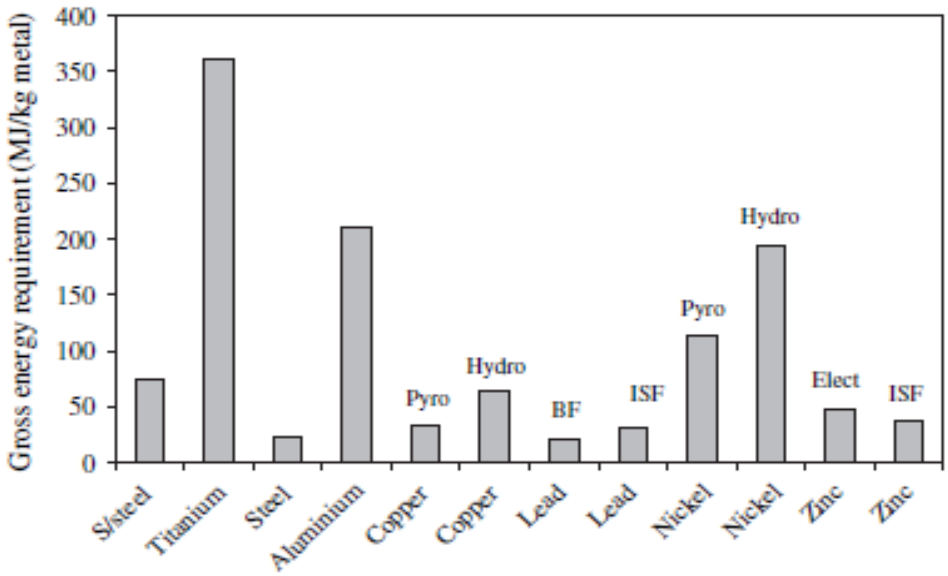

Figure 12: Gross Energy Requirements for various materials (Norgate et. al, 2006).

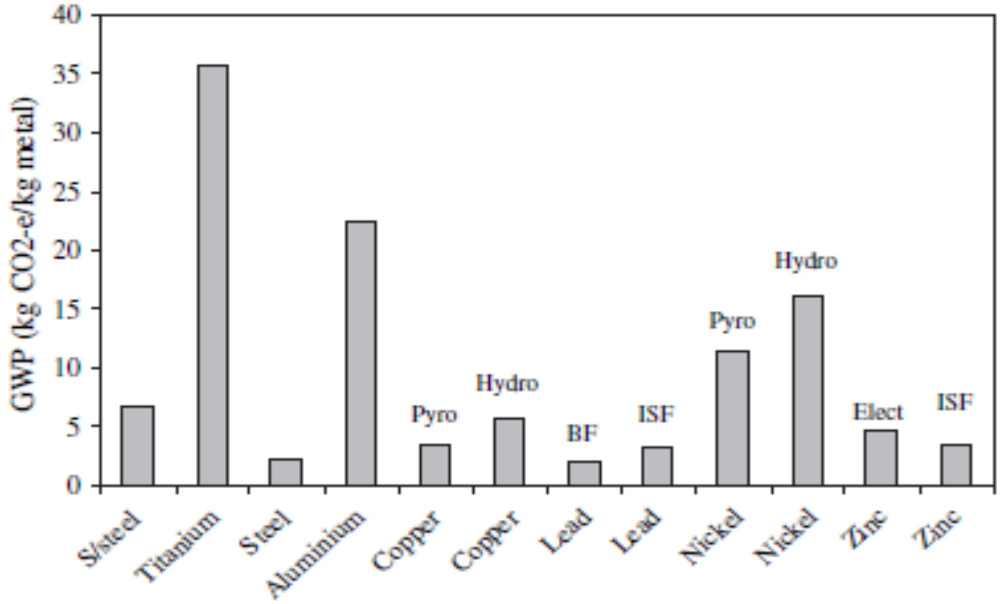

Figure 13: Global Warming Potential of the various materials (Norgate et. al, 2006).

1.5 Barriers to Recycling:

The last two decades have seen a stagnant rate of metals recycling especially for aluminum in the United States (IAI, 2005). The secondary recovery industry has since seen a rise in the United States, motivated by an improving American and Asian economy. This ferrous and non-ferrous metal recycling industry is valued at almost $60 billion in the United States and is continuing to grow. A major trend responsible for this change is the growing demand for products that are manufactured from recycled materials (Usifer, 2012). The outlook for this recycling industry remains positive despite the volatile economies across the globe because of an increase in the demand for scrap materials both by domestic and international consumers and manufacturers (Usifer, 2012; USEPA, 2009). One source (IAI, 2009) predicts the production of aluminum to rise to about 97 million tons by 2020 from the 56 million tons today. Consequently, the secondary aluminum production is also expected to rise from 19 million tons as of today, to about 32 million tons by 2020. Aluminum can be recycled over and over and over again without the loss of its properties. The high volume of aluminum scrap is the main incentive and a major economic impetus for its recycling.

In spite of all the advantages tied to the secondary aluminum recovery industry, there are barriers to recycling that make it a challenging process. Firstly, it starts at the societal level due to the lack of participation in curbside recycling. A study by (Warhurst, 2007) states that numerous policies are in practice that indirectly prevent the growth of the secondary recovery industry, which causes a conflict of interest for recycling materials – (1) the legality to landfill waste is more economical than creating a funding mechanism to promote recycling, (2) funding towards the building of incinerators, (3) manufacturing a non-recyclable product that is cheaper, are some noteworthy points that make it difficult to recycle. Although recycling is still possible despite these, the presence of such policies makes non-recycling options cheaper and easier to execute. The lack of incentives makes it harder for society to recycle and in turn makes it harder to collect the materials to be recycled. Societies, communities and governments should work alongside the industry to effectively collect and separate aluminum products.

A bigger hurdle to recycling aluminum is the compositional uncertainty in the end-of-life material. Recycling such a complex mixture of scrap material not only becomes economically unviable but also becomes compositionally challenging. The accumulation of unwanted material due to contamination in both the collection and processing phases further hampers recycling (Gaustad et al., 2010). However, from a revolutionary standpoint, we are living in a "multi-material" world where a mixture of materials together can fulfill functions not met by just one material. Material use intensity is also decreasing – cans get lighter, cars become smaller, aluminum uses in transportation reduces and the foils used in packaging get thinner and thinner. Sustainability favors such a big change in material use but it also increases the difficulty to collect and recycle aluminum from the end-of-life products.

Another source raises the issue of saturation of sinks or "some products that can use or absorb raw materials, for some recycled raw materials" (Gaustad et al, 2010). The only way secondary production of aluminum can sustain is by increasing the alloy portfolio for secondary production. In fact, other sources have already raised concerns for the limits of the available aluminum alloy sinks for secondary production. In particular, these include aluminum castings (Aluminum Association, AA designation 380) and wrought aluminum can stock (AA designation 3105, 3004 and 3104; Gesing, 2004; Das, 2006; Gaustad et al, 2010). Closed-loop recycling could be a strategy if we want to avoid the unwanted accumulation of scrap from one alloy hindering the recycling process of another. The lack of control over the impurities is what creates a barrier to recycle a mixture of scrap collected from multiple classes of alloy. Another barrier is extracting the impurities during the remelting process. A typical method to remove the impurities in metals is by oxidation. However, there is a thermodynamic barrier to recycling which is illustrated in Figure 14. The figure shows a change in Gibbs free energy as a result of temperature for different metals (Gaustad et al., 2012). It is evident that most of the equilibrium lines for other alloying elements have a higher Gibbs free energy than aluminum. Aluminum is represented by the black line. This means that aluminum is oxidized before the impurities, magnesium and calcium being the only elements that are oxidized before aluminum. A major increase in the secondary recovery industry will only be possible if the above listed barriers to recycling are addressed. Policies that favor an increase in recycling strategies need to be discussed, collection of the scrap needs to be more efficient so that it favors the sorting of the alloy types for increased closed-loop recycling. Decision makers in the secondary recovery industry need a clear picture of the scrap use for the recycling of aluminum. Increased scrap use will ensure minimum cost of production.

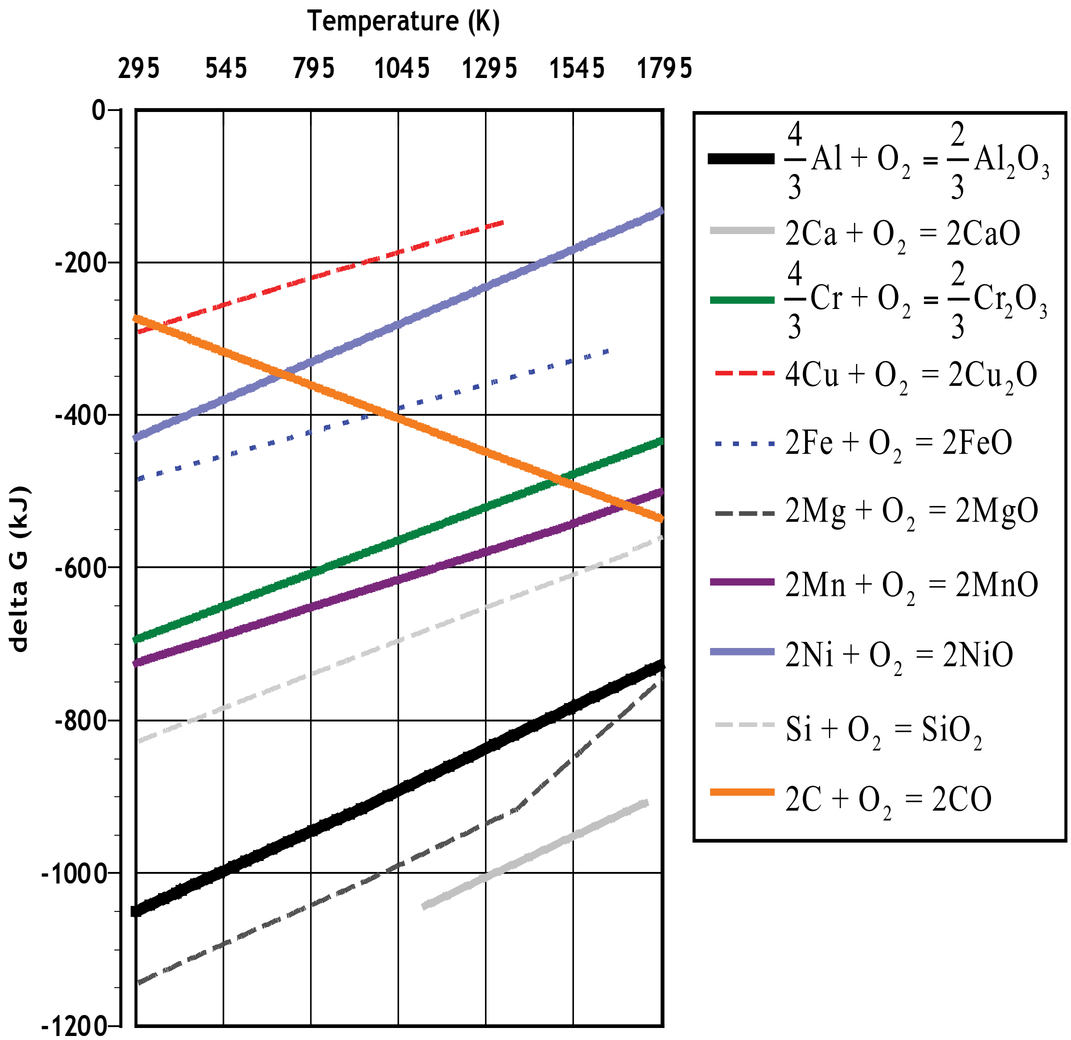

Figure 14: Ellingham diagram depicting the change in Gibbs free energy as a function of temperature for various elements (Gaustad et al., 2012).

2. Hypothesis:

As mentioned previously, one of the main drawbacks in the secondary industry is the accumulation of the unwanted tramp elements in the scrap stream. The alloy producers make use of blending optimization models to help quantify the inputs of raw materials (primary materials, scrap and alloying elements) to manufacture a set of alloys within set specifications. Depending on where someone is positioned in the secondary production industry, there are important decisions to be made about the collection of scrap, sorting and then finally what gets allocated to produce a particular set of alloys (Gaustad et al., 2011). The alloy producers therefore have an important role to play in determining the actual composition of the aluminum products. Although there are specifications that exist, determined by the Aluminum Association (AA), more narrowly defined maximum constraints by the producers often result in reduced scrap use for the production of a given set of alloys. This in turn, leads to an increased production cost and a decrease in environmental savings. This paper explores the trade-offs of using a blending optimization model where property constraints are used instead of the compositional specifications in hopes that this will increase the scrap use, without negatively affecting the performance metrics of the alloys of interest. Property relationships for aluminum and key alloying compositions (magnesium, silicon, iron, copper and lithium) were statistically regressed to create constraints for incorporation in the optimization model calculations. The main focus of this work will be to answer the following question:

Will the replacement of the compositional specifications with property based constraints drive increased scrap use in secondary aluminum production without negatively affecting the performance of the alloys?

3. Methodology

The main aim of this hypothesis is the substitution of property constraints for the compositional specifications in an optimization model that aims at minimizing the production cost of the portfolio of alloys being produced, without negatively affecting the performance of the alloys being produced. The optimization model was created in What's Best, an Excel based linear optimization model. Aluminum alloys from those specified by AA were picked and used for this thesis. Minimum and maximum production specifications were allotted for each and the four key alloying elements (silicon, magnesium, iron and copper) were tracked. We have chosen only to track four main alloying elements that make up the four highest compositions in any aluminum alloy, after aluminum itself. If this work is concluded to be feasible, a larger model can be formulated that is able to track up to twenty alloying elements. Literature research was conducted for the relationships between the properties of aluminum and the compositions of its alloying elements. These relationships were used for regression analysis between two variables – the property of aluminum (dependent variable) and the composition of the alloying element (independent variable). The regression analysis was conducted and an equation established along with a value of the coefficient of determination (R^2). This equation was then incorporated in the optimization model.

3.1 Property-Composition relationships

In this study we are demonstrating the feasibility of substituting property based constraints for the compositional based constraints in hopes that this change will increase the scrap utilization for secondary aluminum production, without negatively affecting the performance criteria. While compositionally based constraints were developed for blending problems based on maintaining certain properties, many have become overly conservative in regards to incorporation of secondary materials. The properties of a material (hardness, ductility, malleability, conductivity etc.) are the most important factor in ensuring end-user functionality. Properties of a material can range from chemical, mechanical, physical or electrical and the end-user functionality can be in one of the many industries like electronics, manufacturing, construction, transportation, aviation etc. One source gave an example of aluminum casting alloy to be used for manufacturing a part. The different casting processes to manufacture the aluminum alloy could be sand casting, permanent mold casting and die casting. The main difference in these processes is the cooling rate – about 0.2 $^oC/s$ for sand casting and about 500 $^oC/s$ for die casting. The higher the cooling rate, the finer is resulting grain size which improves yield strength, fatigue properties and wear resistance. Due to this relationship, die casting produces the best surface finishes and better results. On the other hand, rapid cooling at such high rates could result in a higher degree of porosity. This is a typical example of how choosing a manufacturing process influences the properties of the finished product and its end-user functionality (Dieter, 1997). The idea behind establishing the relationships between the properties of a material and its composition is to make use of these relationships as constraints.

Our case study involves aluminum and hence a few select properties were first chosen and the relationships between the properties and the aluminum alloy compositions were found through literature research. Some of the properties of choice that were selected for this study were – density, elastic modulus, electrical resistivity, dislocation density and melting temperatures. These properties have well known relationships with the compositions of four main alloying elements of aluminum – silicon, magnesium, copper and lithium.

3.1.1 Density and Elastic Modulus

The density and the elastic modulus of aluminum are influenced by the presence of lithium in the alloy, because of lithium's lower density of 0.53 g/cm^3. "Each weight percent of Li decreases the density of Al by 3% and increases the elastic modulus by 6%" (Dieter, 1994). The density of a material is an important characteristic because it directly relates to the mass and volume of an object, two other important physical attributes of any material. For example, in buoyancy, an object with a very high density will sink in to the water, whereas an object with a low density will float. Similarly the modulus of elasticity of aluminum is just as important of a property due to its ability to be deformed. Aluminum, as we know is extremely malleable and ductile which makes it useful for applications of a vast variety. The density of aluminum (~ 2.7 g/cm^3) is the Y-variable (the dependent) that decreases by 3% with an increase in the composition (weight percent) of lithium in aluminum is the X-variable (the independent) (Dieter, 1994). Keeping the standard density of aluminum as the reference data point, other data points could be calculated with every weight percent increase in the lithium composition in aluminum. This relationship between the density and the composition can be hypothesized to be a linear regression. Similarly, the modulus of elasticity of aluminum (~ 70 GPa) is the Y-variable (the dependent) that increases by 6% with every weight percent increase in the composition of lithium in aluminum, which is the X-variable (the independent) (Dieter, 1994). The modulus of elasticity of aluminum was kept as the reference data point. Figure 16 and 17 show the graphical representation of the regression models for the density and elastic modulus of aluminum depending on the composition of lithium.

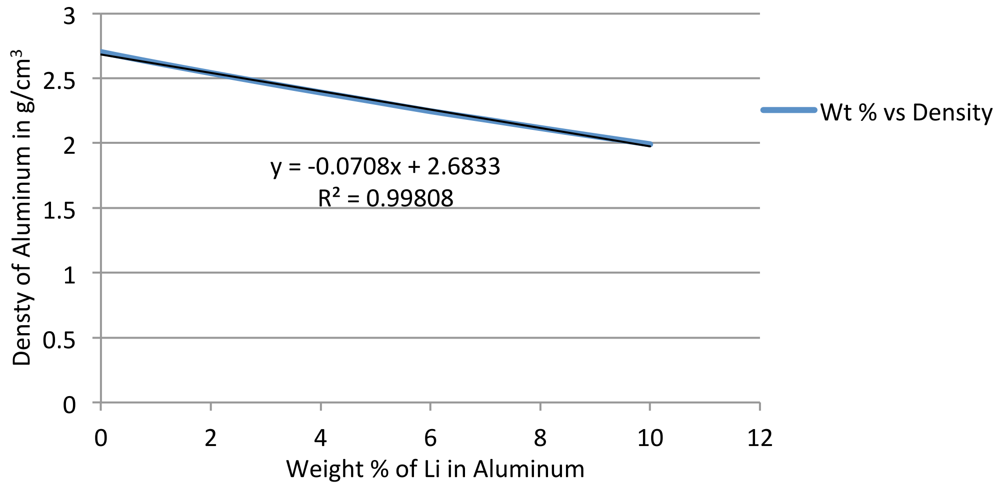

Figure 15: Change in the density of aluminum with the change in composition of Lithium in the alloy (Dieter, 1994).

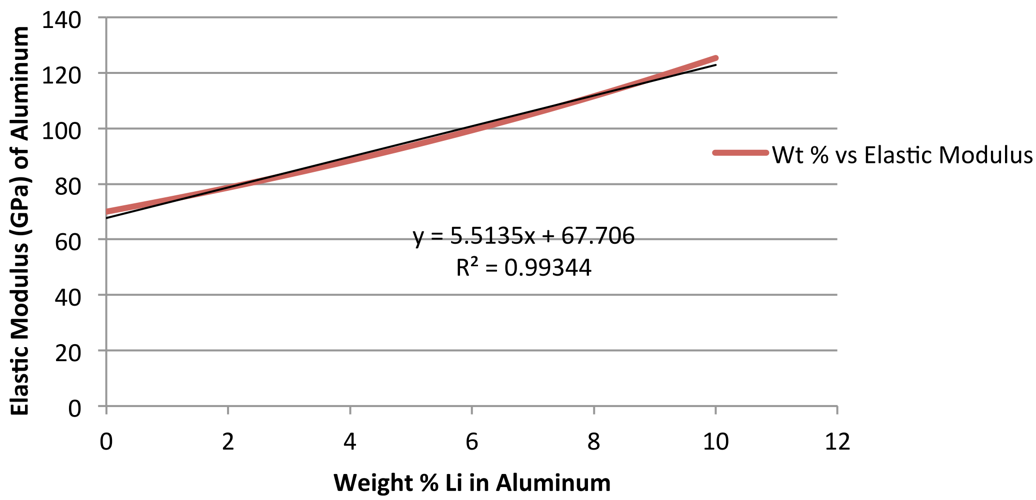

Figure 16: Elastic Modulus of Aluminum with the change in the composition of Lithium in the alloy (Dieter, 1994).

3.1.2 Electrical Resistivity

Resistivity is one of the most important properties of aluminum because of its electrical conductivity that make it viable for various electrical applications like electric water heater, solar panel bodies, automotive, heat exchangers etc. The resistivity together with its lower density than copper makes it a popular choice for long distance power lines. Though its conductivity is only 63% that of copper, its ductility and malleability make up for the drop in conductivity. The electrical resistivity of aluminum depends on the copper content in the alloy. Copper being an excellent conductor of electricity influences the conductivity of a material with its presence. Literature research showed a relationship between the electrical resistivity of aluminum and the composition of copper from one source (Reed-Hill, 1994). A statistical regression was done to analyze the relationship between the underlying variables in question – the electrical resistivity (the dependent) of aluminum and the composition of copper (weight percent) in aluminum (the independent). Literature research provided the data points for this regression analysis which was used to determine the goodness of fit for this model. The statistical significance of the estimated relationship was found to be very close to the actual relationship based on the value of the coefficient of determination. This relationship was then produced as a graph from the data points in the literature research. Figure 18 shows the graphical representation of this data for the dependent variable (electrical resistivity of aluminum) along the Y-axis and the independent variable (composition of copper in Al) on the X-axis.

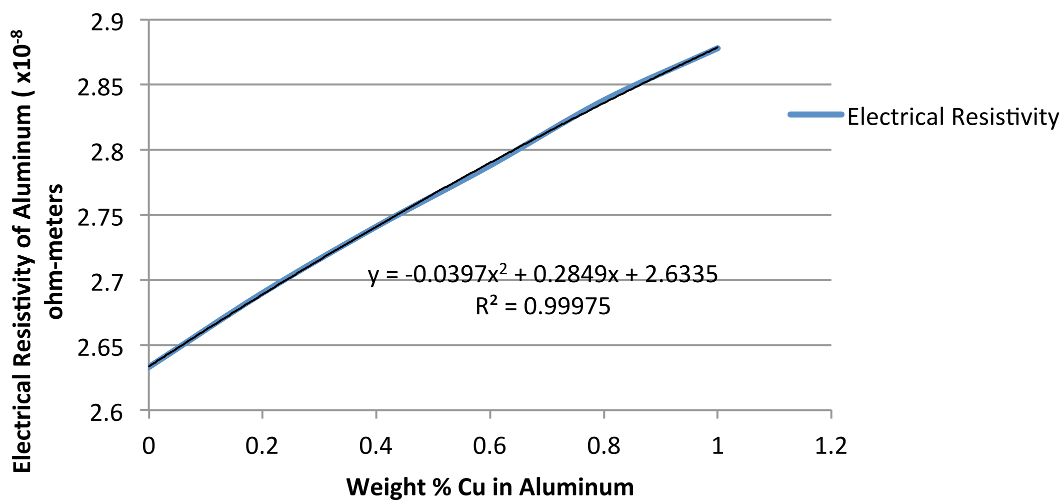

Figure 17: Electrical Resistivity of Aluminum with the change in the composition of Copper in the alloy (Reed-Hill, 1994).

3.1.3 Melting Temperature

Many heat and thermal applications are highly dependent on this property. The melting temperature of various alloys of Al can be changed or altered knowing its relationship with various alloying elements present. To produce such a property-composition relationship, different binary phase diagrams between aluminum and other alloying elements were referred to, data points were established and a regression analysis for these data points was done. The dependent variable here is the melting temperature of aluminum and the independent variable is the composition of the said element in aluminum (Murray, 1985). The referenced data points served as the basis to extrapolate the other data points and create a graphical representation of the relationships and use the same for regression analysis. The diagrams represented mole fraction of the element in aluminum which had to be converted to weight percent in order for the equation to be used in the optimization model. The mole fraction to weight percent conversion was done by first converting the mole fraction to mass fraction and then using the mass fraction to establish the weight percent of the element in aluminum.

$$X_a + X_b = 1 \qquad \text{(Equation 2)}$$

Where,

X_a = mole fraction of element a

X_b = mole fraction of element b.

Mass fractions can be calculated using,

$$\gamma_a = X_a * m_a \qquad \text{(Equation 3)}$$

$$\gamma_b = X_b * m_b \qquad \text{(Equation 4)}$$

Where,

γ_a = Mass of solute a in the solution

γ_b = Mass of solute b in the solution

m_a = molar mass of a

m_b = molar mass of b

Total mass of the solution,

$$(\gamma_{tot}) = \gamma_a + \gamma_b \qquad \text{(Equation 5)}$$

Weight percent,

$$w_a = \frac{\gamma_a}{\gamma_{tot}} * 100 \qquad \text{(Equation 6)}$$

$$w_b = \frac{\gamma_b}{\gamma_{tot}} * 100 \qquad \text{(Equation 7)}$$

Where,

w_a = weight percent of element a

w_b = weight percent of element b.

Given below are the binary phase diagrams and the statistically regressed models with the established relationships. Table 2 gives a summary of the relationship models with their equations that are used in the optimization model.

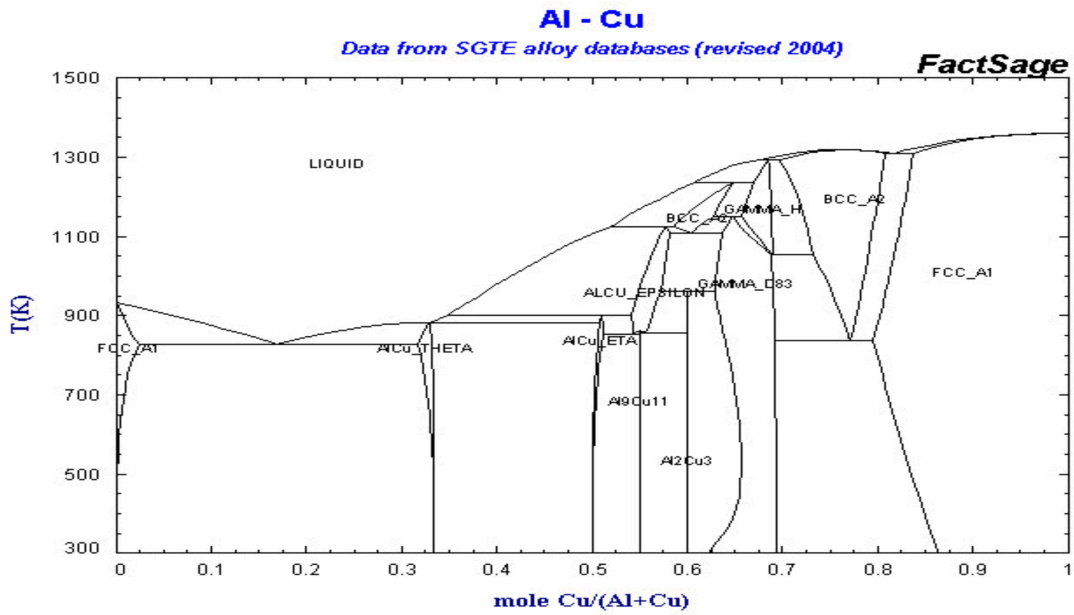

Figure 18: Al-Cu binary phase diagram (SGTE Alloy database, 2004).

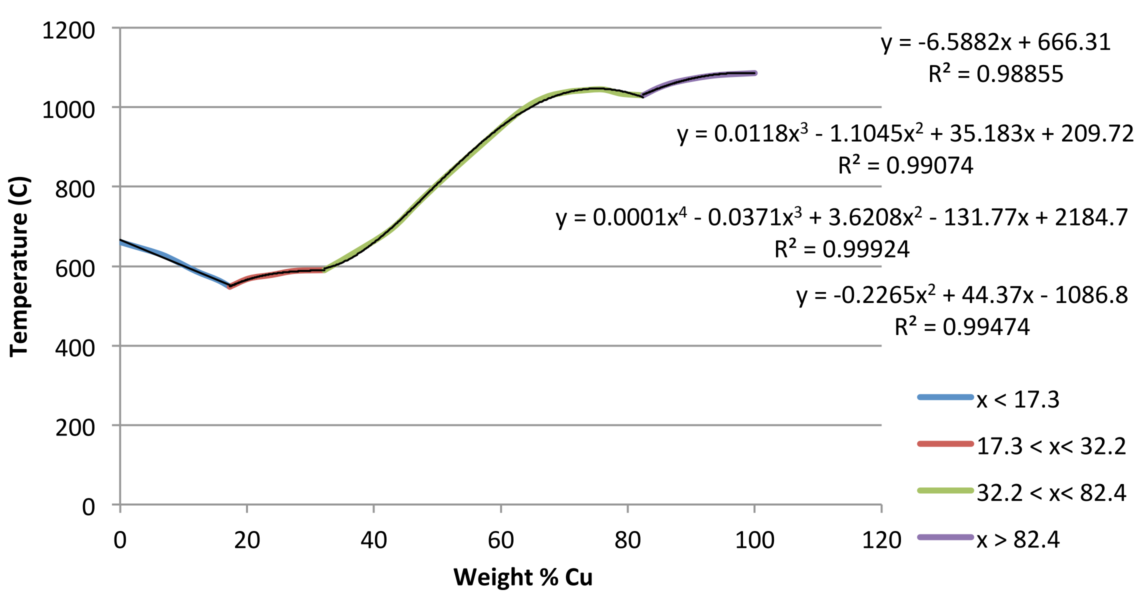

Figure 19: Binary phase diagram of Al-Cu with the solid-liquid phase boundary (Murray, 1985).

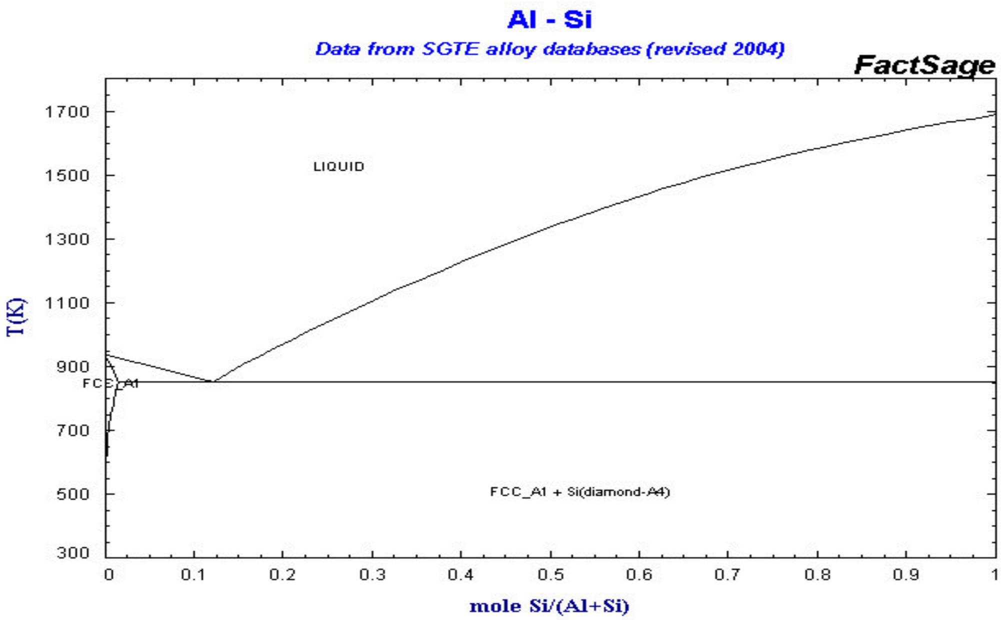

Figure 20: Al-Si binary phase diagram (SGTE Alloy database, 2004).

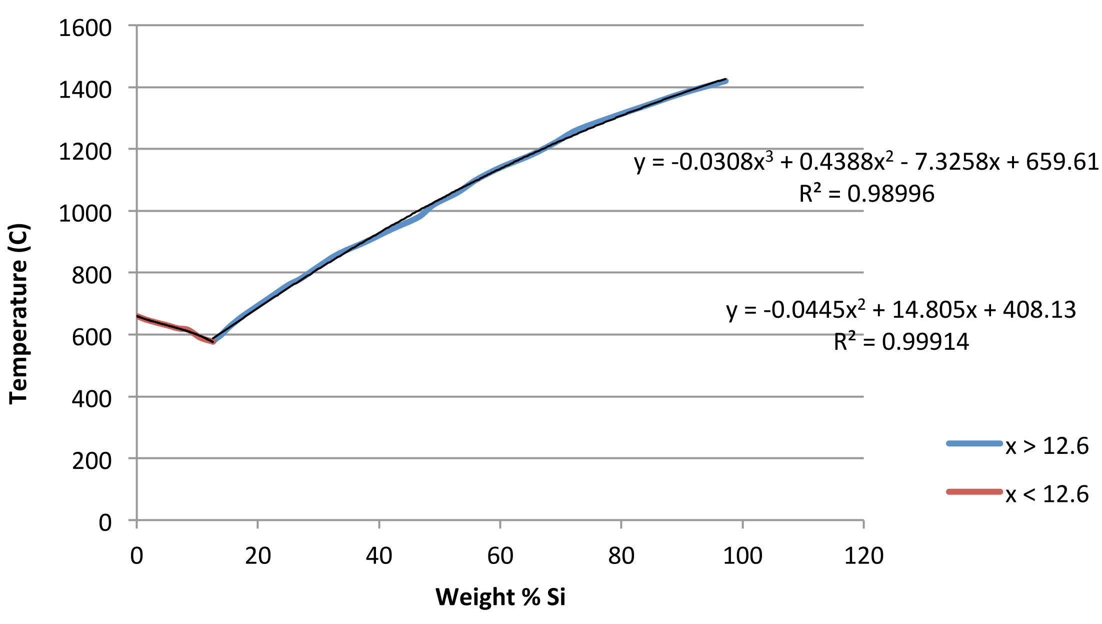

Figure 21: Al-Si binary phase diagram showing the liquid-solid phase boundary (Murray, 1984).

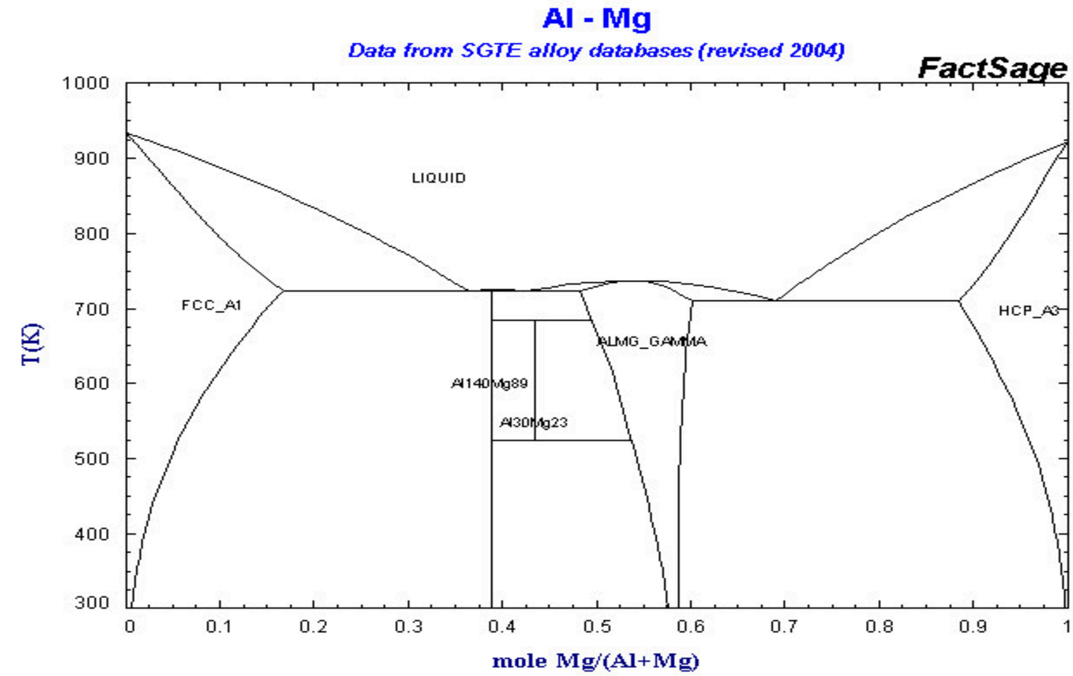

Figure 22: Al-Mg binary phase diagram (SGTE Alloy, 2004).

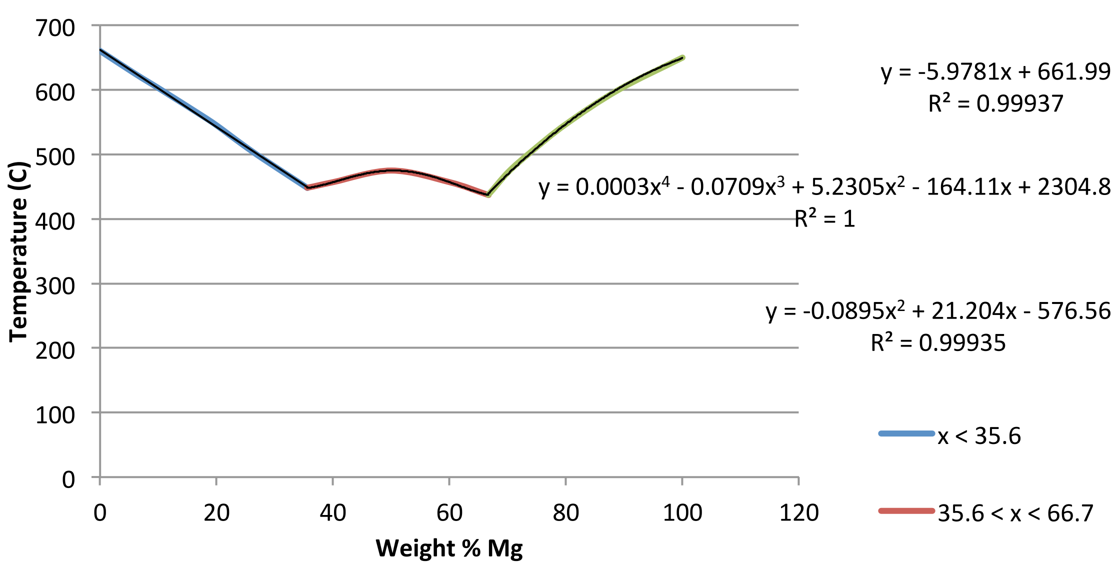

Figure 23: Al-Mg binary phase diagram with the solid-liquid phase boundary (Murray, 1988).

Property	Regression Equation	Bibliography
Density	"Each wt % of Li decreases the density of Al by 3%" **y = -0.0708x + 2.6833, x = wt% Li; y = Density of Al**	(Dieter, 1994)
Elastic Modulus	"Each wt % of Li increases the elastic modulus of Al by 6%" **y = 5.5135x + 67.706, x = wt% Li; y = Elastic Modulus of Al**	(Dieter, 1994)
Electrical resistivity	**y = 0.2451x + 2.6388, x = Wt% Cu; y = Electrical resistivity of Al**	(Reed-Hill, 1994)
Hydrogen Solubility	**Wt% H = exp ((-2691.96/T) – 1.32)**	(Anyalebechi, 1995)
Dislocation Density	**$y = -1E{+}14x^3 + 4E{+}14x^2 - 7E{+}13x + 1E{+}14$ (2nd Order Polynomial), x = Wt% Mg; y = Dislocation Density** **y = 2E+14x + 9E+13, x = Wt% Mg; y = Dislocation Density**	(May et. al., 2007)
Melting Temperature (Al – Cu binary phase diagram)	**For x < 17.3: y = -6.5882x + 666.31, x = Wt% Cu; y = Temperature** **For 17.3 < x < 32.2: $y = 0.0118x^3 - 1.1045x^2 + 35.183x + 209.72$, x = Wt% Cu; y = Temperature** **For 32.2 < x < 82.4: $y = 0.0001x^4 - 0.0371x^3 + 3.6208x^2 - 131.77x + 2184.7$, x = Wt% Cu; y = Temperature** **For x > 82.4: $y = -0.2265x^2 + 44.37x - 1086.8$, x = Wt% Cu; y = Temperature**	(Murray, 1985)
Melting Temperature (Al - Si binary phase diagram)	**For x < 12.6: $y = -0.0308x^3 + 0.4388x^2 - 7.3258x + 659.61$, x = Wt% Si; y = Temperature** **For x > 12.6: $y = -0.0445x^2 + 14.805x + 408.13$, x = Wt% Si; y = Temperature**	(Murray, 1984)
Melting Temperature (Al - Mg binary phase diagram)	**For x < 35.6: y = -5.9781x + 661.99, x = Wt% Mg; y = Temperature** **For 35.6 < x < 66.7: $y = 0.0003x^4 - 0.0709x^3 + 5.2305x^2 - 164.11x + 2304.8$, x = Wt% Mg; y = Temperature** **for x > 66.7; $y = -0.0895x^2 + 21.204x - 576.56$, x = Wt% Mg; y = Temperature**	(Murray, 1988)

Table 2: List of the property-composition relationships for aluminum with various other elements.

3.2 Blending Optimization Model

When gauging the "recyclability" of alloys, it is imperative that a method proficient in performing complex calculations and analysis be devised. Such a method gives a clear picture about the potential of such alloys to be recycled in the form of secondary scrap material. Blending optimization models are mixing software that use the physical compositional data of any material and its alloying elements and batch them according to the specifications put in by the user. They usually operate on compositional constraints to batch the finished alloys. Linear programming models are used by a large number of producers to help support their purchasing and mixing decisions (Lund et. al., 1994). The variety of secondary (recycled) materials available for use by the producers along with the numerous elements relevant to their composition and compositional uncertainty makes it harder to meet the specifications (Gaustad et. al., 2007). The compositional uncertainty leads to batch plans with smaller amounts of secondary materials. These linear optimization techniques make it easier to plan the utilization, buying and sorting of the raw materials and also the upgrading and sorting of the secondary materials (Cosquer and Kirchain, 2003). The optimization model used in this work in particular, addresses the problem of mixing different quantities of raw materials (aluminum scrap, alloying elements and pure aluminum) under certain conditions (minimum production costs, compositional specifications and property constraints) to produce a set of aluminum alloys that is proposed by specifying it's compositional values. The property that a final alloy needs to have is also specified and factored in. To carry out the proposed model using property based constraints, a linear programming optimization software, What's Best! ® 10.0.1.3 by Lindo Systems, Inc. was used. The mathematical definition of this model is given in equations 8-11. The objective function in this model is to minimize the cost of production (Equation 8). Minimizing cost of production also translates to more scrap being used to make the alloy because scraps are generally less expensive than the pure alloying elements and primary aluminum. Equation 9 ensures that raw materials cannot be used in excess of quantities physically available. There is a limited supply of quantities available for production and equation 9 makes sure that the production happens keeping the quantities within the available supply limit. Equation 10 ensures that production meets or exceeds the established target level for each product and ensures mass balance. Each alloy produced is preset with a target production quantity. This equation limits the quantity of the final alloy produced within the specified range, while maintaining the minimum cost production and the limited supply of the quantities of raw material available. Equation 11 ensures that the finished alloy falls between maximum and minimum compositional specifications. Each alloy type has compositional specifications of its alloying elements. These specifications are limits or ranges of weight percent of alloying elements that can be present in the alloys. It is important for the final product to meet these specifications and equation 11 ensures the same.

Minimize: $\sum C_i R_i$ (Equation 8)

Subject to: $\sum x_{ij} = R_i \leq A_i$ (Equation 9)

$D_j^{min} \leq \sum x_{ij} = P_j \leq D_j^{max}$ (Equation 10)

$E_{min} < E_{actual} < E_{max}$ (Equation 11)

Where,

C_i = unit cost of raw material

R_i = amount of raw material, i used to produce the final alloy (in mass units)

A_i = Available amount of raw material, i used to produce the alloy (in mass units)

Dj_{min} = Min amount of the final alloy, j demanded (in mass units)

Dj_{max} = Max amount of the final alloy, j demanded (in mass units)

Pj = Amount of the final alloy, j actually produced.

E_{min} = Min amount of an alloying element supposed to be present in the final alloy

E_{max} = Max amount of an alloying element supposed to be present in the final alloy

E_{actual} = Actual amount (average) of the alloying element present in the final alloy.

3.3 Data and Assumptions:

Optimization models are methods used by many secondary alloy producers to determine the recyclability of any given set of scraps. Closed-loop recycling has been a recurring topic in this work as it is known to be the first choice when trying to recycle any aluminum alloy. Closed loop recycling means gathering scrap from the same industry or a class of alloy that is needed to be produced. For example, to recycle the aluminum used in containers and packaging, scrap from the same industry is collected and recycled to produce alloys that are compositionally close to those that are used to serve the containers and packaging industry. However, secondary alloy producers need to be able to formulate decisions based on alloys that are produced from a wide variety of scrap portfolios. In this work, we have attempted to accomplish this by creating a model that explores mixing raw materials (aluminum scrap, alloying elements and pure aluminum) in order to create a new set of alloys under the property constraints put forth in the model. The scraps chosen to be used in this model represent the three major industries globally where aluminum is used. These are – containers and packaging, automotive and transportation and building and construction. Used beverage cans (UBC) are the scrap aluminum collected from the containers and packaging industry and mainly consist of the alloys that serve this industry. The transportation and automotive industry comprises of mixed auto castings and Cu-Alum radiator scrap. These scraps are predominantly from automotive industry as supposed to the general transportation industry. Wire and cable scrap, mixed turnings and litho sheets are a part of the building and construction scrap. The compositional specifications for this scrap set were established by the European Union standards (ECS 2003). Other alloying elements like iron, magnesium, silicon etc. are also a part of the alloy composition in varying amounts in order to serve a particular end-functionality or a particular industry. For example, alloy 2011 is compositionally different than alloy 2024, even though both alloys belong to the 2xxx series. For the sake of this thesis work however, we decided to track only four of the main contributing alloying elements that make up any given aluminum alloy – silicon, magnesium, iron and copper. These four elements have the highest contributions towards an aluminum alloy apart from aluminum. The prices for this scrap set including the alloying elements were estimated from online sources (Scrap Register, 2014) and do not represent data from any particular firm or organization; these are general scrap prices widely used across the metal.

Alloy	Minimum/Maximum	Production Requirements	Si	Mg	Fe	Cu
2219	Min	10000	0	0	0	0.058
	Max	100000	0.002	0.0002	0.003	0.068
3004	Min	20000	0	0.008	0	0
	Max	120000	0.003	0.013	0.007	0.0025
4032	Min	15000	0.11	0.008	0	0.005
	Max	100000	0.135	0.013	0.01	0.013
5052	Min	25000	0	0.022	0	0
	Max	100000	0.0025	0.028	0.004	0.001
6061	Min	25000	0.004	0.007	0	0.0015
	Max	150000	0.008	0.012	0.007	0.004
7075	Min	15000	0	0.021	0	0.012
	Max	100000	0.004	0.029	0.005	0.02

Table 3: Production requirements of the final alloys (AA, 2007).

To avoid any problems arising from a restricted supply of raw materials, we assumed that all the raw material and scraps were available in unlimited quantities. For the sake of the optimization model in this work, however, the available scrap had to be quantified. The final sets of alloys were created on a maximum production scale of 100,000 lbs. per set except for alloys

3004 and 6061 which had a maximum production scale of 120,000 lbs. and 150,000 lbs. respectively, totaling the final production portfolio to 670,000 lbs. for the entire set. Since we calculated the final results assuming an unlimited supply of the raw materials, they are also independent of the production scale. The final sets of alloys to be produced were selected from the six predominant series of aluminum alloys as described and set by the Aluminum Association (AA). The final set of alloys to be produced were – 2219 from the 2xxx series, 3004 from the 3xxx series, 4032 from the 4xxx series, 5052 from the 5xxx, 6061 from the 6xxx series and finally, 7075 from the 7xxx series. We specified a minimum and a maximum amount of each alloy to be produced to show a realistic approach to the mixing model evaluation. A minimum production value of the alloy was specified to make sure that all the alloys were produced. Pure aluminum was also made available to ensure that the compositional specifications could be met.

4. Results and Discussion

4.1 Base Case Results

The optimization model evaluates the potential of the scrap material utilization in producing a set of new aluminum alloys (2219, 3004, 4032, 5052, 6061 and 7075). These sets of alloys are currently available as end-market alloys with specifications set by the Aluminum Association (AA).

	2219	**3004**	**4032**	**5052**	**6061**	**7075**
UBC	0	20000	13198	12326	24955	14667
Mixed auto castings	0	0	0	0	0	0
Cu- alum radiator	2255	0	157	0	0	0
Wire and cable scrap	444	0	0	12294	0	0
Mixed turnings	0	0	0	0	0	0
Litho sheets	2639	0	0	0	0	0
Si	0	0	1645	0	45	0
Mg	0	0	0	380	0	174
Fe	0	0	0	0	0	0
Cu	0	0	0	0	0	160
Al	4661	0	0	0	0	0

Table 4: Primary results of the optimization model showing the amount of scrap and alloying elements used for each alloy (in lbs.)

Table 4 shows the trend in the amounts of scrap used in the production of each individual alloy. As seen in table 4, different alloys require different quantities of scrap for their production. The potential of an alloy to use scrap for its production is called its recycle friendliness (Gaustad et. al, 2010). Scrap prices are lower than the primary alloying elements which drive the minimization of the production costs. Consequently, the objective function of this model was to minimize the production cost due to which the scrap use was at its highest. Alloy 3004 was produced with a 100% scrap, making it the most recycle friendly alloy. Within its 100% scrap use, it is interesting to notice that all of its scrap came from one source – UBC (used beverage cans). This aligns with the uses of most of the alloys in the 3xxx series as their major use is in the containers and the packaging industry. One source confirms that the three main alloys used in the packaging industry are the 3000 series with manganese being its main alloying element, the 5000 series with magnesium being the man alloying element and the 1000 series which is a high purity aluminum alloy with the alloying elements making up only 1% of the total composition and the rest 99% is pure aluminum (Terukina, 2013).

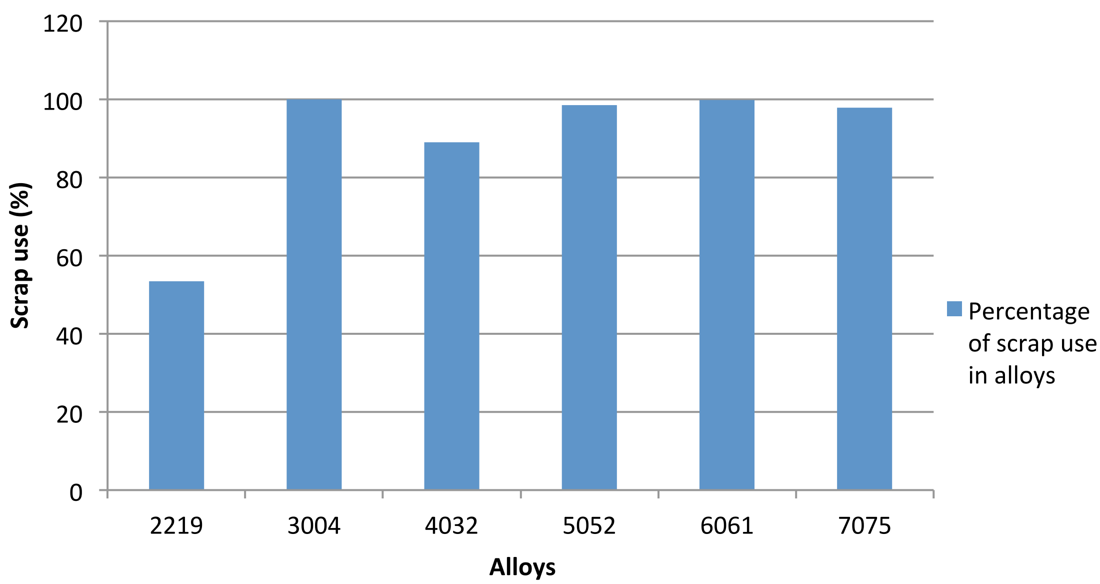

Figure 24: Percentage of scrap use for each alloy.

Used beverage cans make up a majority share of the scrap available in the United States (IAI, 2009). This is evident from the scrap use numbers in Table 4 as most of the scrap that is used to produce each alloy comes from the UBCs. Except 2219, all the other alloys use at least 60% or more of the scrap coming in from the UBCs. All the alloys that were produced had a very high scrap use percentage, mainly within the range of 85-100% except for 2219 that only had about 53%, as seen in figure 24. It was outperformed by every other alloy, in terms of scrap use by at least 150% or more.

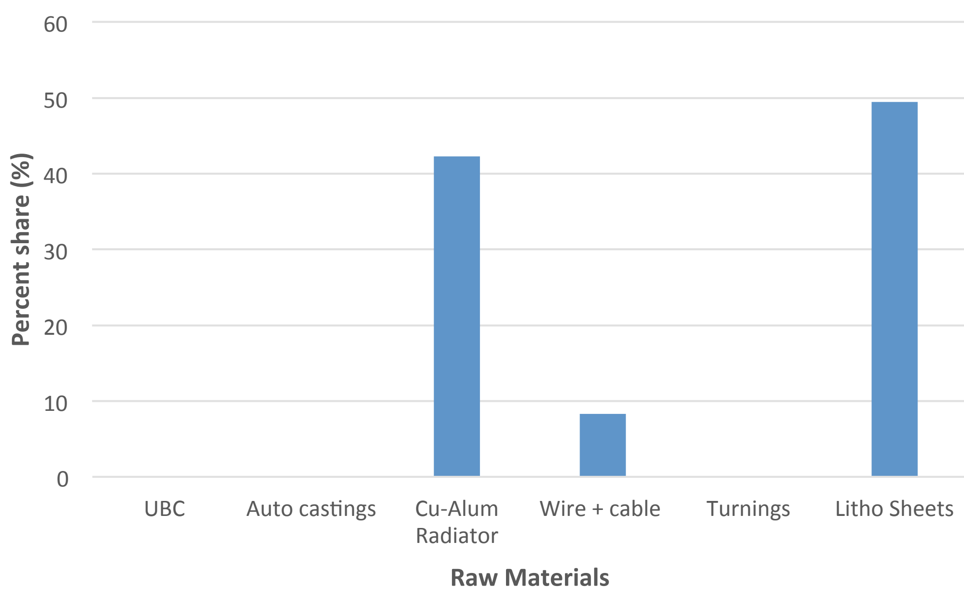

Figure 25: Percentage share of each raw material to the total scrap use in 2219.

2219 is the only alloy that doesn't use any UBC in its production; the main reason being that 2219 is mostly used for high temperature applications (Terukina, 2013). Its main alloying element is copper that helps harden the alloy to make it favorable for applications in the automotive industry and construction. Surprisingly, litho sheets make up for almost 50% of the scrap used in 2219. Litho sheets mainly make use of alloys from the 3000 series and the 1000 series or a combination of both. Since their main use is in lithography, their compositional make-up is mostly pure aluminum with minor amounts of the alloying elements. As mentioned earlier, most of the 3000 series is used in packaging and beverage cans. This goes to show that the amount of scrap used for a particular alloy not only depends on the compositional specifications of that alloy but also the available scrap portfolio. Extrapolating this information, it is quite possible that the end-user functionality of an alloy can also be greatly affected by the scrap that goes into making them. It can be concluded that in the case of 2219, the scrap portfolio that is available also affects the scrap used to make the same class (or series) of alloys. Another acute observation is that auto-castings were not used in producing any of the alloys. One can make the argument that due to the presence of high amounts of iron in the automotive scraps, their accumulation poses a barrier to the recycling and further hampers the potential of those scraps from being used in the process (Gaustad et. al, 2010).

4.2 Property-constraints results

The main theme of this work was to postulate increased scrap use in the production of a set of alloys by exploring property based constraints for the aluminum specifications instead of the compositional constraints. This was done by conducting literature research on pre-existing relationships between certain properties of aluminum and the alloying element that affected the said property. Once the literature search was done, the equations were regressed and analyzed for their goodness of fit. We used this equation to run the optimization model and notice any changes in the scrap use.

4.2.1 Electrical Resistivity vs. Copper

	2219	**3004**	**4032**	**5052**	**6061**	**7075**
UBC	0	16370	11289	23234	20181	13956
Mixed auto castings	0	0	0	0	0	0
Cu- alum radiator	5460	3551	1725	0	4764	0
Wire and cable scrap	444	0	0	0	0	0
Mixed turnings	0	0	0	0	0	0
Litho sheets	0	0	0	0	0	0
Si	0	0	1648	0	55	0
Mg	0	0	0	321	0	177
Fe	0	0	0	0	0	0
Cu	0	79	338	1445	0	867
Al	4095	0	0	0	0	0

Table 5: Scrap use for Electrical Resistivity of aluminum versus copper content (in lbs).

A glance at table 5 shows some changes in numbers from the base case results. Electrical Resistivity of aluminum is one of the most important properties not just for aluminum but for every other metal (ferrous or non-ferrous). The relationship between the resistivity of aluminum and copper was factored in the model in the form of an equation produced from the regression analysis.

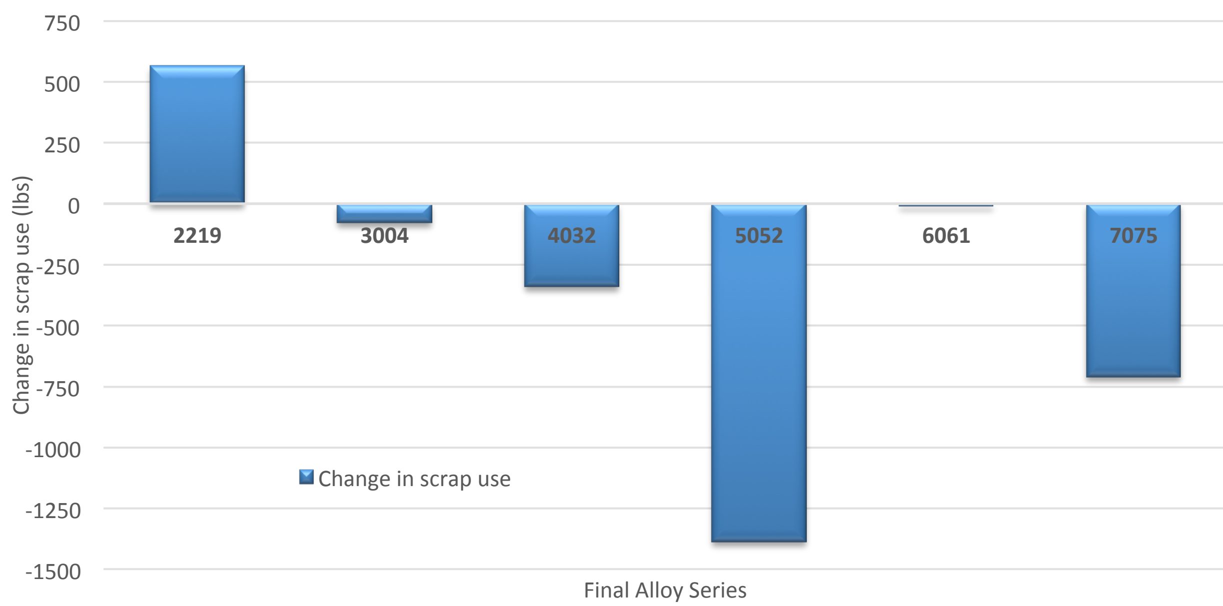

Figure 26: Change in scrap use for electrical resistivity (in lbs).

As seen in Figure 26, alloy 2219 is the only one with an increase in the scrap use by almost 6%. Every other alloy incurred a loss in the scrap use. The main reason for this could be that copper is its main alloying element. 2219 is used extensively in the automotive and construction industry. Due to copper being the main alloying element, not only is its electrical resistivity affected but also its strength and hardness. The primary functionality for this alloy is to deliver the strong, hard characteristics in its use and for that, the copper present in the alloy is the alpha-element. This could be the reason for the increased scrap use in 2219. One more observation that is worth noticing is that all of the litho sheets used for the base case results have been compensated by the use of the Cu-Alum radiator. Such a big drop in percentage (50 % to 0 %) is definitely worth contemplating upon. One could assume that the use of litho sheets in the base case results was impractical, except to fulfil the compositional gap needed to produce the alloy. What was unexpected is that the wire and cable scrap had no change at all, despite the high tension uses of 2219 for construction.

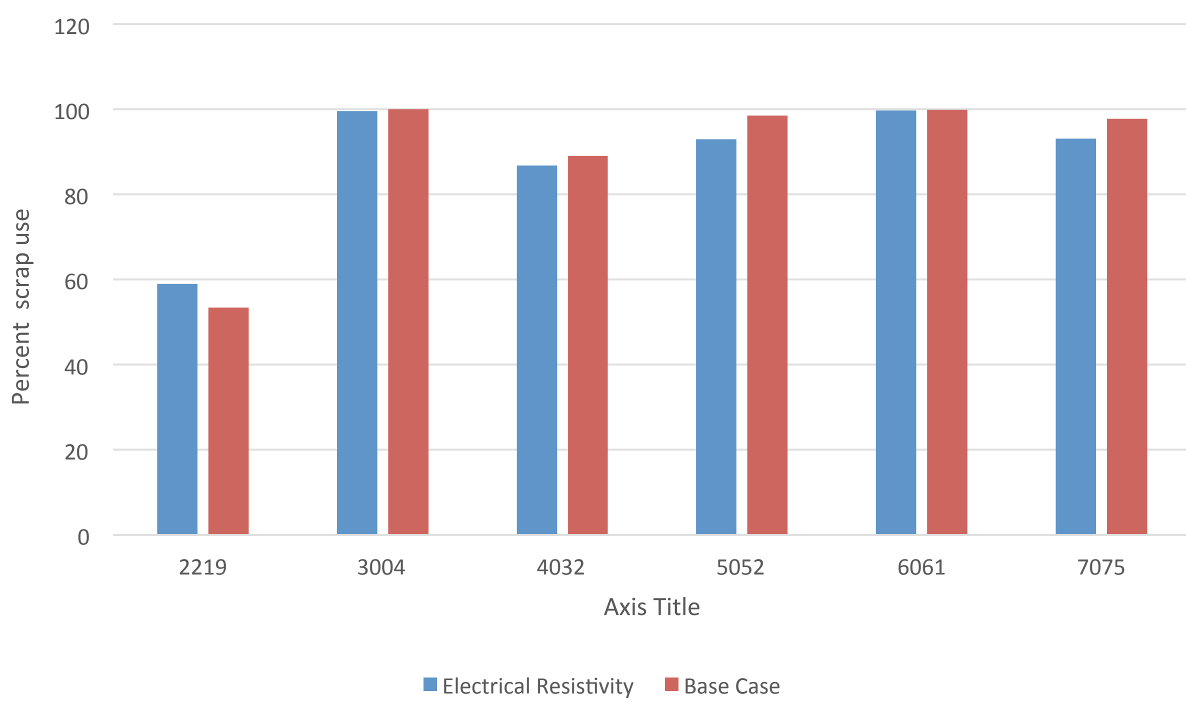

Figure 27: Comparison between the base case and electrical resistivity scrap use (in %).

3004 and 6061 had a scrap use drop under 1%. Alloys 4032 and 7075 had a drop of almost 3.5-4%. The biggest drop was seen in 5052 with almost 8% less scrap being used than the base results. A very astute observation is that alloys 3004, 4032, 5052 and 7075 all increased their use of pure copper as an alloying element, which was expected because of the decrease in the overall scrap use. Figure 27, above, shows the change in the scrap use percentage for the base case and property constraints.

4.2.2 Melting Temperature

4.2.2.1 Copper

	2219	**3004**	**4032**	**5052**	**6061**	**7075**
UBC	0	199926	13319	24659	24862	14811
Mixed auto castings	0	0	0	0	0	0
Cu- alum radiator	4667	74	37	0	92	0
Wire and cable scrap	444	0	0	0	0	0
Mixed turnings	0	0	0	0	0	0
Litho sheets	654	0	0	0	0	0
Si	0	0	0	0	45	0
Mg	0	0	380	314	0	173
Fe	0	0	0	0	0	0
Cu	0	0	0	27	0	16
Al	4235	0	0	0	0	0

Table 6: Scrap use after factoring in the melting temperature relationship with the copper content (in lbs).

Melting temperature can greatly affect the grain boundaries and alter the physical structure of any material. These grain boundaries can be clearly visible along the binary phase diagrams. The relationship between the melting temperature of aluminum and its copper content was drawn from its binary phase diagram and plotted into Excel. This relationship was used to drive the optimization model. Table 6 shows the amounts of raw material and alloying elements used to produce each alloy. Alloy 2219 shows an overall increase in the scrap use with most of it coming from the Cu-Alum radiator. Contributions from the wire and cable scrap and litho sheets were present but insignificant compared to that from the Cu-Alum radiator. As seen in the previous cases of the base case results and the electrical resistivity, UBC and mixed auto-castings provided no contribution to the scrap use even with the melting temperature. In the base case results, we saw all the scrap use for 3004 coming from UBC, but for melting temperature 74.4 lbs came from the Cu-Alum radiator. Even though UBC wasn't the only scrap used to produce 3004, the overall scrap use remains at 100%. Alloy 4032 used mostly UBC with minor contributions from pure Mg and Cu-Alum radiator. We saw Si being used for 4032 in the base case results because the Si specifications are at 11-13.5% and the second highest specification coming from magnesium 0.8-1.3%. Although, after factoring in the melting temperature property constraint, Si was not used in the production at all, but magnesium contributed about 380.2 lbs. Alloy 5052 saw a slight increase in the scrap use as well. Compared to the base case results, the use of UBC almost doubled up in the case of 5052, compensating for the wire and cable scrap while the wire and cable scrap was not used at all. We saw no change in the scrap use for 6061 but a slight increase of about 145 lbs for 7075. The overall scrap use for the entire portfolio was higher than the base case results. Factoring in the property here did make an impact on the scrap use. This is visible in Figures 28 and 29 where we see the amount of scrap increase for each alloy and a comparison with the scrap use in the base case results.

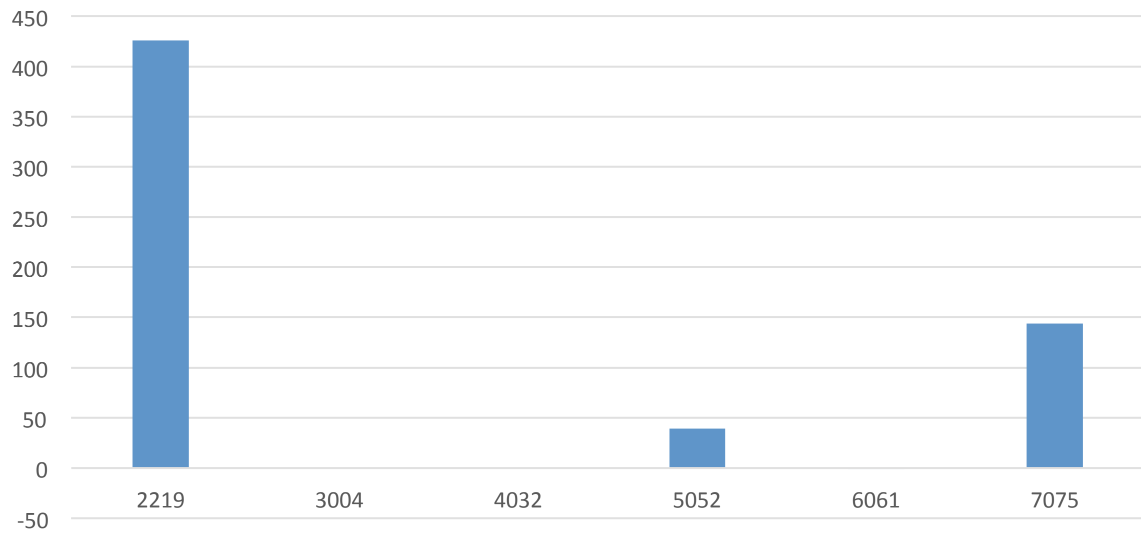

Figure 28: Amount of scrap use for melting temperature of aluminum vs copper content (in lbs).

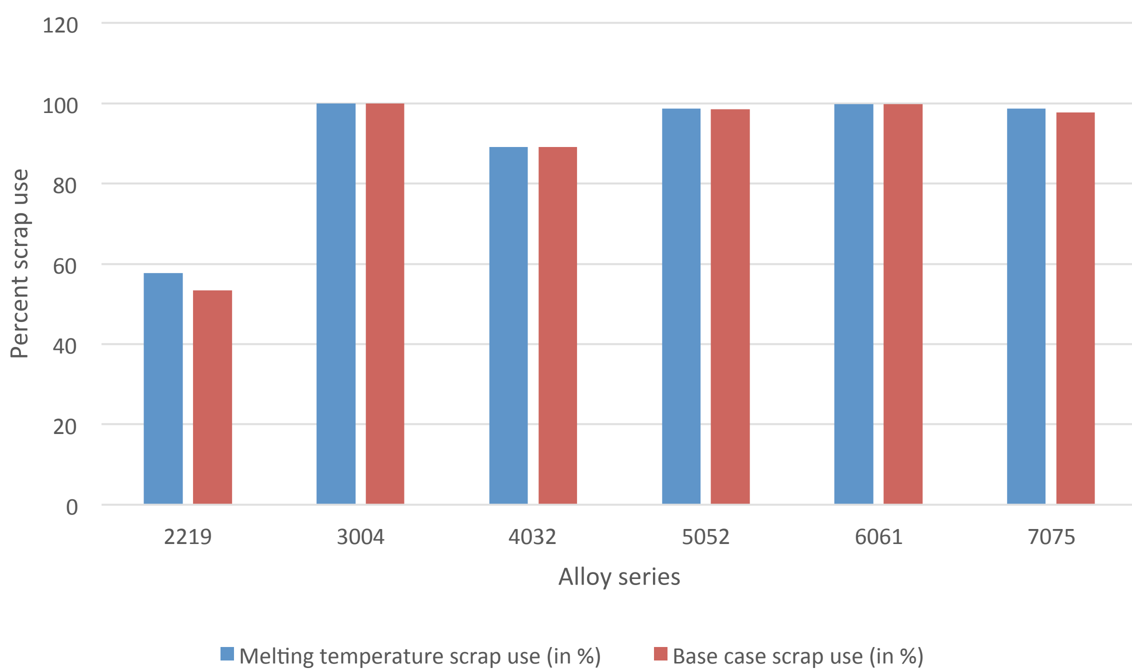

Figure 29: Scrap use comparison between base case and melting temperature (in %).

4.2.2.2 Silicon

	2219	3004	4032	5052	6061	7075
UBC	0	19588	14518	10144	24485	14358
Mixed auto castings	0	0	0	0	0	0
Cu- alum radiator	2252	0	172	0	0	0
Wire and cable scrap	181	0	0	13945	0	0
Mixed turnings	0	0	0	0	0	0
Litho sheets	2580	0	0	0	0	0
Si	237	412	310	519	515	308
Mg	0	0	0	392	0	175
Fe	0	0	0	0	0	0
Cu	0	0	0	0	0	158
Al	4750	0	0	0	0	0

Table 7: Amount of scrap used for the melting temperature vs silicon content (in lbs).

Factoring in the relationship between the melting temperature and silicon content, one trend that is obvious in Table 7 is the use of the alloying element silicon to meet the compositional specifications of the final alloy. The only increase in scrap use is seen in alloy 4032; one of the reasons being the high silicon content (11-13.5%) and the relationship between the melting temperatures versus silicon content turning out to be favorable to the production of 4032. Another trend we see that has been consistent through all the previous cases is the absence of the auto castings in the production of any of the alloys. It is surprising for the case of 2219 because mixed auto castings contain about 9-10% of silicon. The use of pure silicon for 2219 is expected because of the relationship of the property with the silicon content. 236.7 lbs of silicon are used to meet the specifications. On one hand, it is not a big share of the material use, but on the other, it is the first time we have seen silicon being used for 2219. Going back to the previous point of the mixed auto castings containing a large portion of silicon, it is worth contemplating as to why mixed auto castings did not get used to make up for the extra silicon content for the production of 2219 instead of pure silicon. One might argue that the collection of the scrap may hamper the use of auto-castings for its silicon content. As mentioned before, the unwanted accumulation of scrap and alloying elements can hinder the process of recycling. The same might be the case for the absence of the use of auto-castings for the production of alloy 2219. Alloy 2219 still does not have any UBC in its production. It does, however, have a mix of multiple scraps for this particular property constraint. We saw mostly Cu-Alum and Litho sheets being used previously but for this case we have contributions from the wire and cable scrap, litho sheets, pure aluminum and also silicon. Also, alloy 3004 has fallen below the normal 100% scrap use we have seen in the previous cases. The first thought again going to the use of pure silicon to make up for the compositional specification. Another observation that is noteworthy is the large amount of wire and cable scrap that is used by alloy 5052 as compared to the melting temperature and electrical resistivity versus the copper content, both of which used none of the wire and cable scrap for 5052. The base case results did, however use a substantial amount of the wire and cable scrap.

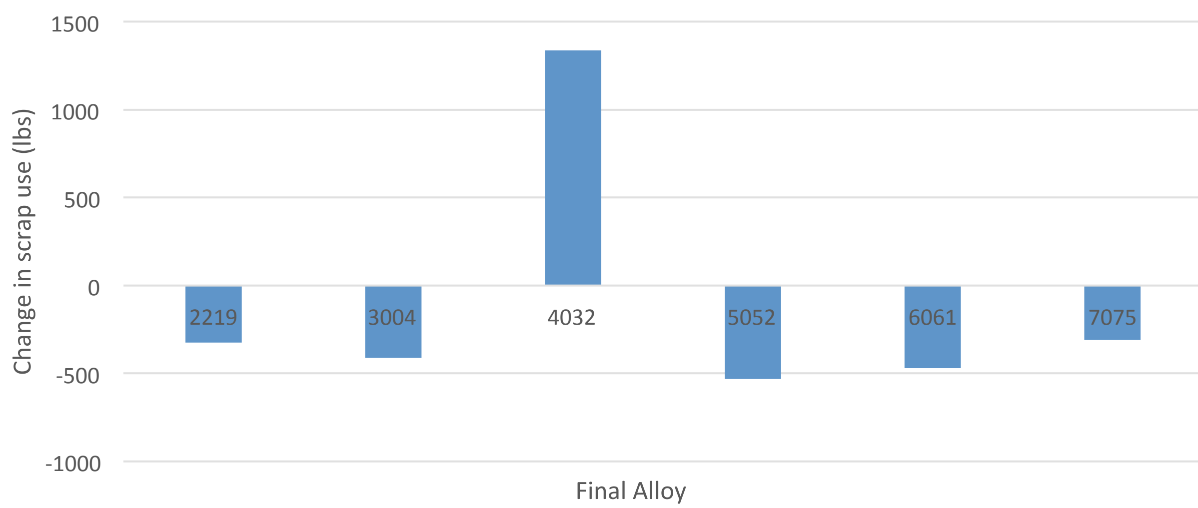

Figure 30: Amount of scrap use for the melting temperature versus silicon content (lbs).

Both 6061 and 7075 also saw a reduction in their scrap use. 6061 compensated this decrease in scrap use with the use of pure silicon whereas 7075 used pure silicon, magnesium and copper to compensate for the drop in scrap. Figure 30 shows the amounts of scrap change. As mentioned before, 4032 saw an increase in scrap use by almost 1350 lbs whereas every other alloy saw a decrease in their potential scrap use. 2219, 3004, 6061 and 7075 used between 250-400 lbs less scrap. Alloy 5052 was the only alloy to have decreased in scrap use by more than 500 lbs. Overall conclusions says that the melting temperature of aluminum versus the silicon content is only favorable for alloy 4032. Figure 31 shows the comparison between the scrap percent use for the base case and the property constraint.

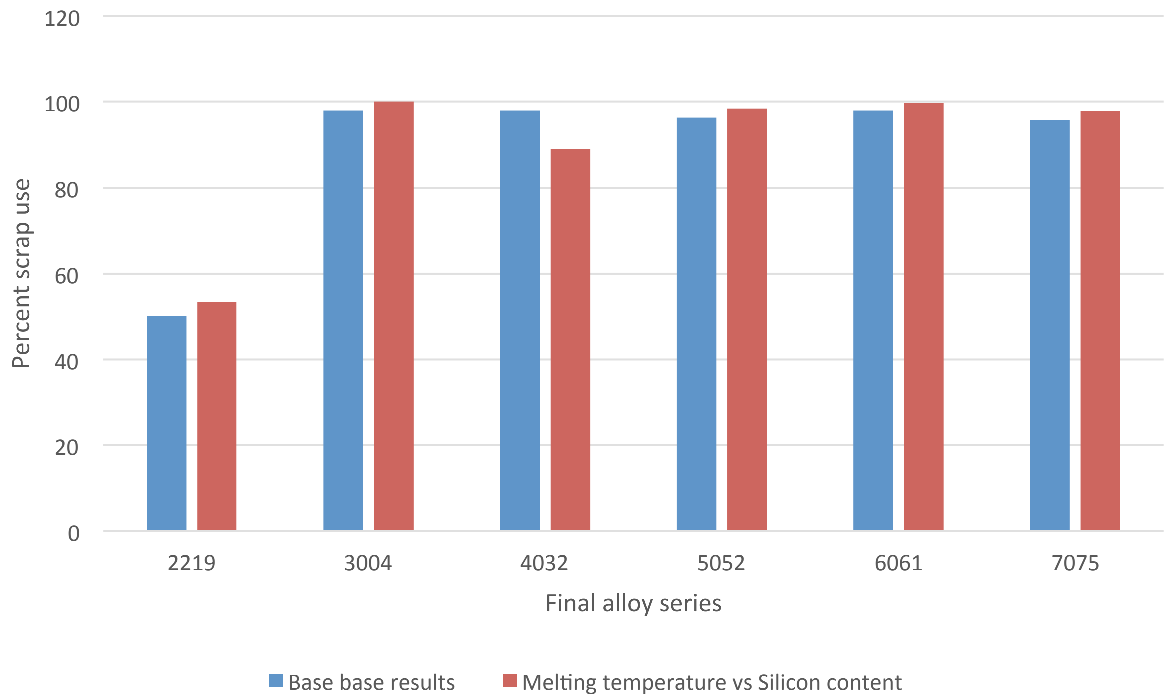

Figure 31: Percent scrap use comparison between base case and the property constraint (in %).

4.2.2.3 Magnesium

	2219	**3004**	**4032**	**5052**	**6061**	**7075**
UBC	0	20000	13198	13889	24955	14472
Mixed auto castings	0	0	0	0	0	0
Cu- alum radiator	0	0	157	0	0	573
Wire and cable scrap	9024	0	0	11111	0	0
Mixed turnings	0	0	0	0	0	0
Litho sheets	0	0	0	0	0	0
Si	0	0	1645	0	44	0
Mg	0	0	0	0	0	0
Fe	0	0	0	0	0	0
Cu	585	0	0	0	0	0
Al	390	0	0	0	0	0

Table 8: Amount of scrap used for property constraint of melting temperature vs Mg content (in lbs).

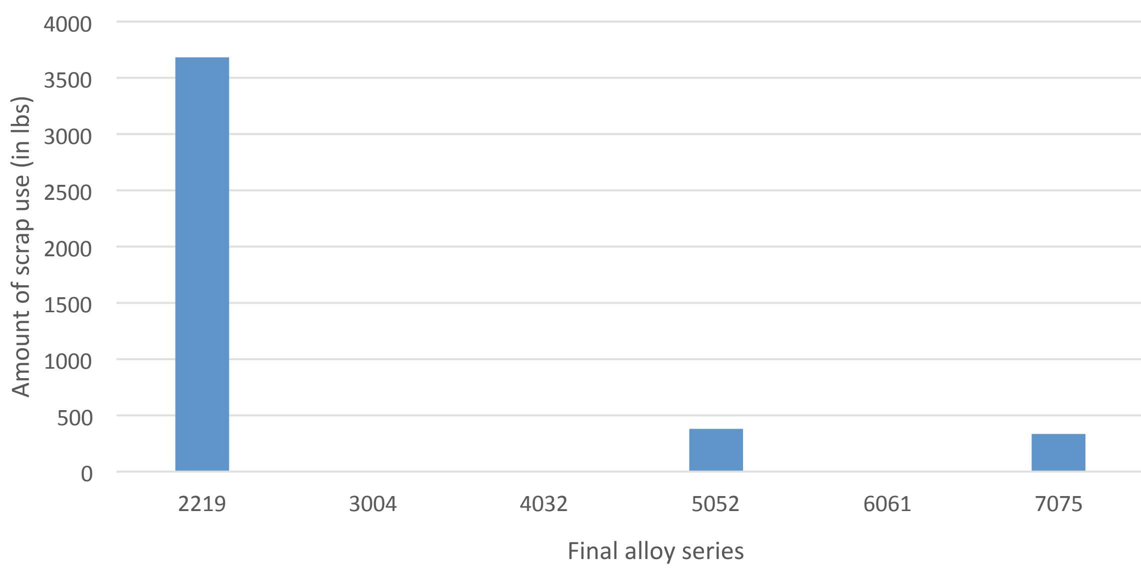

Figure 32: Change in the amount of scrap used for the production of each alloy (lbs).

Melting temperature of aluminum versus the magnesium content shows the best results as compared to the other melting temperature relationships. All of the alloys either stayed the same in numbers for scrap use or showed an increase. Alloy 2219 stands out with almost 3700 lbs of increase in scrap. What is also astonishing is that this is the only case where none of the Cu-Alum radiator scrap was used in 2219. Most of the scrap increase came from the wire and cable scrap and the drastically compensated pure aluminum. It did see a 27% increase in its scrap use as compared to the base case results as is seen in Figure 32 and 33. Alloy 2219 crossed the 90 % mark for the first time in this work, including the base case results. Alloys 5052 and 7075 also saw a jump in their scrap use with 5052 increasing almost by 400 lbs and 7075 increasing by about 350 lbs. The overall trend in the entire alloy portfolio is positive in its scrap use.

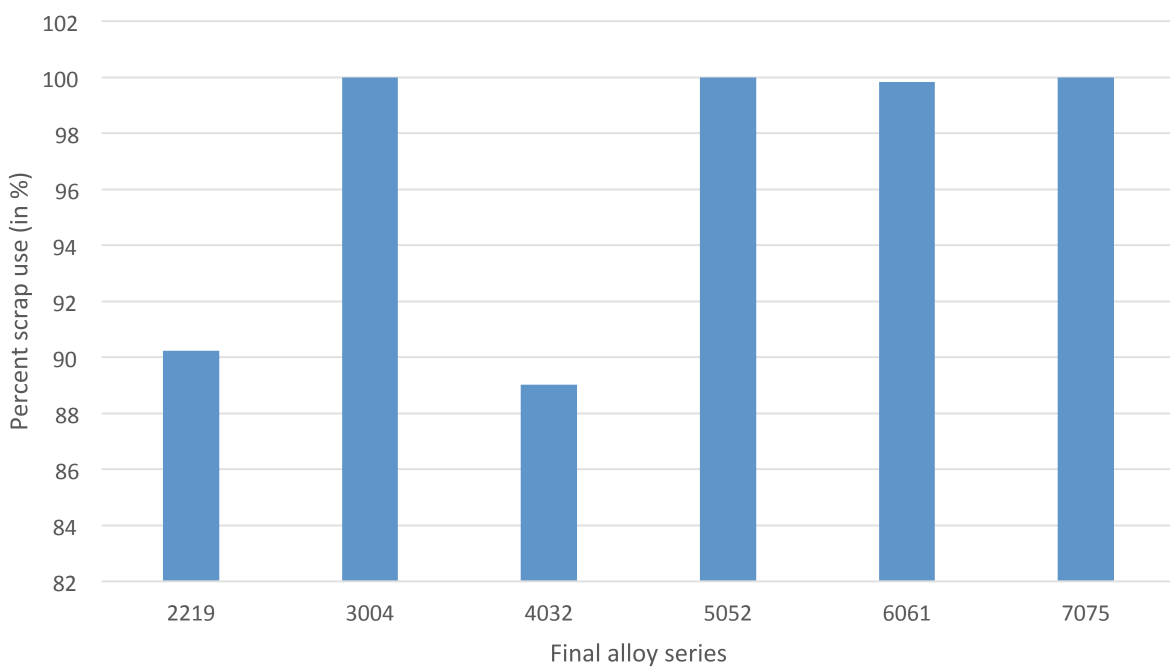

Figure 33: Percent scrap use for each alloy (%).

Although we didn't see a change of scrap use in 3004, 4032 or 6061, we didn't see a drop in the scrap use either. 3004 maintained its consistency with a 100% scrap use but 5052 and 7075 both also used 100 % scrap in their production. 4032 and 6061 maintained their scrap use at 89% and 99 % respectively. This relationship between the melting temperatures versus the magnesium content proved to be very favorable for alloys 2219, 5052 and 7075.

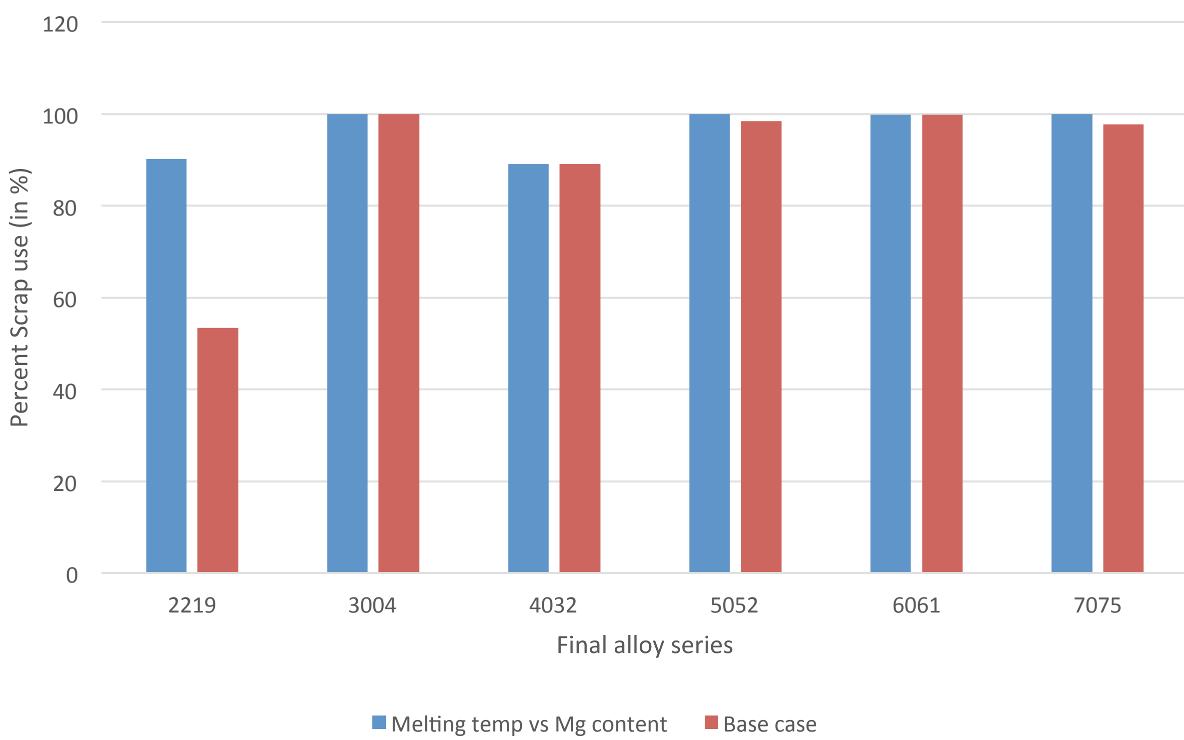

Figure 34: Comparison of percent scrap use between the property constraint and base case (%).

4.3 Sensitivity Analysis

The results show how the scrap portfolio affects the scrap use for the alloys produced. Scrap from the packaging industry (Used Beverage Cans) was highly utilized due to the extremely low undesirable accumulation (Gaustad et al. 2010) whereas scrap from the automotive market was used in least amounts. It is evident from this observation that the potential to use scrap highly depends on the availability of the scrap to the alloy producers. Although the range of the operational settings like the available scrap and alloying elements can prove helpful in the decision making process, a detailed analysis of what target modifications need to be made is very important. Alloy producers explore the use of this information provided by shadow prices to aim for a more profitable modification to any given alloy. Shadow prices quantify the sensitivity of the optimal result to changes in the constraints. Shadow price can be defined as "the value of the change in the objective function at the optimum for a unit change in that constraint." (Gaustad et al. 2010).

$$SP_{constraint} = \frac{\delta(Objective\ Function)}{\delta\ (Constraint)} \qquad (Equation\ 12)$$

Slack Variables are constant values that are added to an inequality to fulfil constraint. These values can be either zero or non-zero. The closer a value is to zero, the greater is the effect of that constraint on the overall function. Both the shadow prices and the slack values are used to make decisions based on specific modifications that will yield a more profitable outcome. Tables 9 and 10 give the shadow prices of both the base case results and the resistivity vs. copper content.

Element	Constraint	Alloy	Shadow Price
Mg	Max	2219	195.5
Fe	Max	2219	156.6
Cu	Max	5052	142.4
Mg	Min	5052	1.74
Cu	Max	2219	1.25

Table 9: Shadow prices for base case results.

Element	Constraint	Alloy	Shadow Price
Fe	Max	2219	228.6
Mg	Max	2219	195.5
Fe	Max	2219	156.6
Mg	Max	2219	147.6
Cu	Max	5052	141.4

Table 10: Shadow Prices for Copper vs. Resistivity.

What is interesting to see is that the shadow price for copper drops when the property constraint is introduced.

Tables 11 and 12 below show the slack values of the elements and the constraints. Copper is the element that has the biggest effect on the objective function in both the cases and has a value closest to zero.

Element	Constraint	Alloy	Slack Value
Cu	Min	6061	0.15
Mg	Min	2219	2
Cu	Min	5052	2.5
Si	Max	2219	3.3
Fe	Max	5052	15

Table 11: Slack Values for base case results.

Element	Constraint	Alloy	Slack Value
Cu	Min	6061	0.15
Si	Min	2219	0.8
Si	Max	5052	1.4
Mg	Min	2219	2
Si	Max	2219	3.3

Table 12: Slack Values for Copper vs. Resistivity

5. Conclusions:

Aluminum recycling is beneficial for the present industrial sustainability and will also be beneficial for the future generations. Collection programs need to be encouraged and logistically placed in order to drive an increase in the aluminum recycling programs. As it has been mentioned before, the difference in the energy use between primary and secondary aluminum is almost 90% savings. To ensure a sustained use of the limited energy resources, it is very crucial to shift our attention to secondary aluminum industry. This will be possible with an increased use of scrap in aluminum production. Not only will this be an economical benefit, but it will greatly reduce impacts on the environment and our energy sources. This strategy will ensure a life-long aluminum production and increase the recycling rate. Mixing decisions for the new alloy productions will have to rely heavily on the repeated use of aluminum scrap. One source (IAI, 2009) estimates that the demand for aluminum will only increase for the foreseeable future and the recycling rates will remain stagnant, extrapolating from the current recycling practices. It estimates the amount of aluminum in use to have increased from about 90 million tons in 1970's to about 600 million tons today and to cross the 1 billion ton mark by 2020. These numbers not only raise concerns for our current recycling practices but also cultivate a strong need to shift to the secondary aluminum industry. The author of this work has attempted to exhibit the benefits of redesigning alloys to accommodate more scrap by the use of a modelling framework. To address the above listed barriers to recycle aluminum with an increased scrap use, this work has hypothesized the use of property constraints in the optimization modelling to increase the scrap use for an alloy production. By using an optimization model to evaluate the production of alloys, this work has (1) evaluated the trade-offs between using property constraints and compositional constraints, (2) shown the abilities of certain alloys to accommodate more scrap in its portfolio and (3) acknowledged the effective changes needed to be made during the production of an alloy to increase its ability to include more scrap. As such, this work is an extended version of the previous studies on secondary production of aluminum alloys with the help of an optimization modelling framework (Gaustad et. al, 2012; Gaustad and Kirchain, 2007; Gaustad et. al, 2010). It specifically explores the idea of using property constraints to drive an increased scrap use, using optimization modelling while keeping the production costs at a minimum.

The base case results of the optimization model showed that the alloy production used between 85-100% of the scrap across its portfolio with the exception being 2219 which only used about 53%. Once we introduced the property constraints, there was a noticeable change in the numbers. In some cases, we saw a significant increase in the scrap use, in some cases there was a drop and some others there was no change. The properties of interest were – electrical resistivity versus the copper content, melting temperature versus copper, silicon and magnesium content and the dislocation density versus the magnesium content. The electrical resistivity of copper showed an increase in scrap utilization for 2219 while the other alloys decreased their utilization of scrap for production. 2219 increased its scrap utilization to almost 60%, which was an increase by 7%. Similarly, the melting temperature based on the composition of copper, silicon and magnesium showed an increase in scrap utilization for alloys 2219, 4032, 5052 and 7075 in the case of copper, alloy 4032 in the case of silicon and alloys 2219, 5052 and 7075 in the case of magnesium.

Although we saw improvements in scrap utilization in some cases, there was no uniformity in the results. The scrap utilization was random. A few pointers to be noted here are – (1) it shows that there is a scope to drive increased scrap utilization by using property constraints, (2) alloy producers can now dive deep into the results of the scrap portfolio used to produce the given set of alloys, (3) the scrap utilization is loosely dependent on the kinds of scrap available, the compositional specs of those scraps and the compositional specs of the final alloys being produced. These different case analyses show that there is possibility to increase the secondary material utilization during design process of new alloys while staying within the compositional limits that have been established. The optimization model used in this study is designed to be used for a production portfolio that is not limited to this case. It can be extrapolated to track up to 20 alloying elements and is independent of the production scales of the final alloys without making any additional changes to the constraints or the equations. Not only is this model user friendly, but it also is currently in use by some metallurgists and alloy producers. Being extendable for use to a more complex mixing problem, a model like this not only holds promise for future in-depth analysis of material recycling but also makes way for future studies that involve more than one class of material.

6. Future Work:

Having shown that the property constraints can drive increased scrap use in some cases, we have established a basis for a more in-depth analysis of this study. Metallurgists and alloy producers make use of decision variables to increase the recyclability of an alloy. The recycling strategies in the industry today need to be reevaluated in order to ensure that we see an increase in the scrap utilization in the future. This action can only start at an individual level addressing issues like better scrap collection systems, socio-economic benefits explained by the government and acting on the same to increase use of scrap in the secondary production of aluminum. The merger between the intentions of the government on this issue and the social involvement to enhance the quality of this system is one way metallurgists can ensure a secondary production industry can increase its output in the future. Another major factor worth exploring, that could enhance the utilization of scrap during the secondary production phase is closed-loop recycling. Closed-loop systems use the scrap from one particular sector to produce alloys for the same sector. This ensures maximum utilization of the scrap. What hinders this process is the collection system and the sorting process. Overlapping of the collected scrap from one sector to another means a bigger mixture of the alloying elements and impurities. If and when these issues are addressed, there will certainly be an increase in the secondary production.

Further studies will be needed to establish a smooth and efficient recycling system. Although this work shows that the property-composition relationships used in the linear programming helps in the increased scrap use, future work will evaluate if these are practical to be included in the recycling industry. Metallurgists and alloy producers can extend their analysis to exploring other properties of aluminum alloys that can be incorporated into the optimization model to boost the utilization of scrap. Physical properties like the ductility and malleability, strength versus the alloying elemental compositions and chemical properties like density and conductivity can be evaluated to give a detailed insight of the recyclability of a particular alloy or scrap. Modifying these property-compositional relationships to fit a model can be very advantageous to the increase in scrap use. Success in this area can give way to detailed sensitivity analysis. Sensitivity analysis in detail will help metallurgists in choosing which modifications to target in order to achieve maximum recyclability of the alloy. Tightening or loosening some concentrations might drive more scrap to be used for that particular alloy which in turn will lower the cost of production. Sensitivity analysis can indirectly improve production processes to produce alloys with highest recycling content and also the lowest amount of primary aluminum possible. Primary aluminum increases production costs and also burdens the environment with extra energy that goes into producing it. The Aluminum Association predicts that a ton of aluminum that is recycled saves the same amount of energy as 24 barrels of crude oil, 15 tons of water, 9 tons of CO_2 emissions and 2.5 tons of solid waste (AA, 2011 and Terukina 2013).

The case study explored the use of property constraints for aluminum specifications to evaluate the possibility of using such constraints in optimization models to increase the scrap that goes into the secondary production of aluminum. This study paves way for future work in the field of metallurgy and material science; to understand the complexity of aspects pertaining to alloy redesign. The model used in this can also prove to be a great asset for metallurgists and alloy producers. Expansion of this work in the future may be possible for other classes of materials like glass, ferrous and other non-ferrous materials.

7. References:

Abbaschian, Reza and Robert Reed-Hill. "Physical Metallurgy Principles." 3rd Edition. PWS Publishing Company, Boston, 1994.

Alcoa, Inc. "Aluminum Smelting." Online at http://www.alcoa.com/global/en/about_alcoa/pdf/Smeltingpaper.pdf. Accessed 11th March 2013.

Alcoa, Inc. et al. "How Aluminum is Produced." Webpage, online at http://www.rocksandminerals.com/aluminum/process.htm. Accessed 13th March, 2013.

Anyalebechi, Prince N. "Analysis of the Effects of Alloying Elements on Hydrogen Solubility in Liquid Aluminum Alloys." Scripta Metallurgica et Materialia, 1995. Vol. 33, issue 8, pp 1209 – 1216.

Ayres, Robert U. "Metals Recycling: Economic and Environmental Implications." *Resources, Conservation and Recycling, July 1997*. Vol. 21, pp. 145 – 173.

Boin, U.M.J. and M. Bertram. "Melting Standardized Aluminum Scrap: A Mass Balance Model for Europe." Journal of Materials, 2005. Pp. 26 – 33.

Carroll, Mark C. "Improvements to the Strength and Corrosion Resistance of Al-Mg-Mn Alloys of near AA – 5083 chemistry." Ph.D. Dissertation, Materials Science and Engineering, Ohio State University, Columbus, Ohio, 2001. Document 30222456, adviser – Glenn S. Daehn. Pages 271.

Cosquer, A and Randolph Kirchain. "Optimizing the Reuse of Light Metals from End-of-Life Vehicles: Lessons from Closed-loop Simulations." *TMS: The Minerals, Metals and Materials Society, 2003*. Taken from the Annual TMS meeting in San Diego, California, March 2-6, 2003 (Automotive Alloys Symposium).

Das, Subodh K. "Designing Aluminum Alloys for a Recycle Friendly World." Materials Science Forum, 2006. Vol. 519 – 521, pp. 1239-1244.

Dieter, George E. "Relationship between Materials Selection and Processing." *ASM International, 1997*. Vol. 20, pp. 297 – 308.

Gaustad, Gabrielle, Preston Li and Randolph Kirchain. "Modelling Methods for Managing Raw Material Compositional Uncertainty in Alloy Production." Resources, Conservation and Recycling, 2007. Vol. 52, pp. 180 – 207.

Gaustad, Gabrielle, Elsa Olivetti and Randolph Kirchain. "Design for Recycling: Evaluation and Efficient Alloy Modification." Journal of Industrial Ecology, 2010. Vol. 14, pp. 286 – 308.

Gaustad, Gabrielle et al. "Towards Sustainable Material Usage: Evaluating the Importance of Market Motivated Agency in Modelling Material Flows." Environmental Science and Technology, 2011. Vol. 45, issue 9, pp. 4110-4117.

Gaustad, Gabrielle et al. "Improving Aluminum Recycling: A Survey of Sorting and Impurity Removal Technologies." Resources Conservation and Recycling, 2012. Vol. 58, pp. 79-87.

Gerasimov, V.V and V.V Gerasimova. "Effects of Alloying on the Mechanical Properties of Metals." Metal Science and Heat Treatment, 1993. Vol. 35, issue 5, pp. 177 – 180.

Global Resources Consumption per capita per day. Sustainable Europe Research Institute, 2004. Online at http://www.materialflows.net/trends/analyses-1980-2008/material-consumption-per-capita-and-day-in-2004/ (Accessed 27 July 2012).

Guo-Feng, Li, et al. "Effects of Retrogression Heating Rate on Microstructures and Mechanical Properties of Aluminum Alloy 7050." Transactions of Nonferrous Metals Society of China, 2010. Vol. 20, issue 6, pp. 935 - 941.

Hatayama, H et al. "Dynamic Substance Flow Analysis of Aluminum and its Alloying Elements." Materials Transactions, 2007. Vol. 48, Issue 9, pp. 2518 – 2524.

International Aluminum Institute. “Aluminum for Future Generations: Sustainability Update 2005.” Online at http://www.world-aluminium.org/media/filer_public/2013/01/15/fl0000132.pdf. Accessed 28th December, 2013.

International Aluminum Institute. “Global Aluminum Recycling: A Cornerstone of Sustainable Development.” 2009. Online at http://www.world-aluminium.org/media/filer_public/2013/01/15/fl0000181.pdf. Accessed 15th October, 2013.

Kaufman, J.G. et al. “Aluminum Alloy Castings: Properties, Processes and Applications.” ASM International, Materials Park, Ohio, 2004. ISBN: 0871708035.

Kelly, Thomas D and Grecia Matos. “Historical Statistics for Mineral and Material Commodities in United States.” Unites States Geological Survey, 2006. Online at http://minerals.usgs.gov/ds/2005/140/. Accessed 7th Janurary 2014.

Kim, J.Y., et al. “Aging characteristics of recycled ACSR wires for distribution lines.” Electrical Insulation Conference and Electrical Manufacturing and Coil Winding Conference, Rosemont, IL. 22-25 September, 1997.

Li, Preston, et al. “Identifying Economic and Scrap Reuse Benefits of Light Metals Sorting Technologies.” The Minerals, Metals and Materials Society, EPD Congress, 2005.

Lund, J.R. et al. “Linear Programming for Analysis of Material Recovery Facilities.” Journal of Environmental Engineering, 1994. Vol. 120, issue 5, pp. 1082 – 1094.

Malarvizhi, S and V Balasubramanian. “Effects of Welding Processes on AA2219 Aluminum Alloy Joint Properties.” Transactions of Nonferrous Metals Society of China, 2011. Vol. 21, issue 5, pp. 962 – 973.

Martchek, K.J. “The Importance of Recycling to the Environmental Profile of Metal Products.” 4th International Symposium on Recycling of Metals and Engineered Materials; TMS, 2000.

Matos, Grecia and Lorie Wagner. "Consumption of Materials in the United States." Annual Review of the Energy and Environment, 1998. Vol. 23, pp. 107-122.

Matthews, Emily, et al. "The Weight of Nations: Material Outflows from Industrial Economies." World Resources Institute Report, September 2000.

May, J., et al. "Mechanical Properties, Dislocation Density and Grain Structure of Ultrafine-Grained Aluminum and Aluminum-Magnesium Alloys." Metallurgical and Materials Transactions A, 2007. Vol. 38, issue 9, pp. 1941-1945.

Mondolfo, L.F. "Aluminum Alloys: Structure and Properties." Butterworth's Publication, London, 1976. Volume 5.

Murray, J.L. and McAlister A.J. Aluminum-Silicon Binary Phase Diagram. Alloy Phase Diagrams, vol. 3, ASM Handbook, ASM International, 1984.

Murray, J.L. Aluminum-Copper Binary Phase Diagram. Alloy Phase Diagrams, vol. 3, ASM Handbook, ASM International, 1985.

Murray, J.L. Aluminum-Magnesium Binary Phase Diagram. Alloy Phase Diagrams, vol. 3, ASM Handbook, ASM International, 1988.

Nikam, P, et al. "Composition Dependence of Electrical Properties of Al-Sb Thin Films." Bulletin of Materials Science, 1997. Vol. 20, issue 7, pp. 1015-1021.

Norgate, T. E., S. Jahanshahi and W. J. Rankin. "Assessing the Environmental Impact of Metal Production Processes." Science Direct, Journal of Cleaner Production, 2006. Vol. 15, Issue 2, pp. 838-848.

Norgate, T. E. and W. J. Rankin. "Greenhouse Gas Emissions from Aluminum Production: A Life Cycle Approach." Metallurgical Society of the Canadian Institute of Mining, Metallurgy and Petroleum; Proceedings of the International Symposium on Greenhouse Gases in the Metallurgical Industries: Policies, Abatement and Treatment, 2001. Pp 275 – 290.

Nriagu, Jerome O. "A Silent Epidemic of Environmental Poisoning." Environmental Pollution, 1988. Vol. 50, pp. 139-161.

Reed-Hill, Robert E and Reza Abbaschian. "Physical Metallurgy Principles." 3rd Edition. 1994. PWS Publishing Company, Boston, MA.

Rotem, A, et al. "Correlation among Microstructure, Strength and Electrical Conductivity of Cu-Ni-Be Alloy." Metallurgical and Materials Transactions, 1988. Vol. 19, issue 9, pp. 2279 – 2285.

Schaefer, Florian, et al. "Ecological Footprint and Biocapacity." Eurostat; Environment and Energy, 2006.

Scrap Register. Online at http://www.scrapregister.com/metal-price/aluminum-scrap/7 (Accessed April 2014).

SERI, FoEE and Global 2000. 2013. Hidden Impacts: How Europe's Resource Overconsumption Promotes Global Land Conflicts. Vienna and Brussels.

Sheehan, Bill Ph.D. "Zero Waste, Recycling and Climate Change." Grass Roots Recycling Network, October 2000. Online at http://www.grrn.org/page/zero-waste-and-climate-change (Accessed January 2013).

Sustainable Europe Research Institute, SERI. "Global Resources Consumption per capita per day." 2004. Online at http://www.materialflows.net/home/ (Accessed June 2012).

Tenekedjiev, Ned, et al. "Microstructures and Thermal Analysis of Strontium-treated Aluminum-Silicon Alloys." American Foundrymen's Society, Des Plaines, IL, 1995.

Terukina, Andres Tominga. "Barriers and solutions to closed-loop aluminum beverage can recycling." Department of Hydraulic and Environmental Engineering, Norwegian University of Science and Technology, Trondheim. Thesis for Master's in Industrial Ecology, 2013.

UNEP, 2010. "Assessing the Environmental Impacts of Consumption and Production: A report of the working group on the Environmental Impacts of Products and Materials to the International Panel for Sustainable Resource Management, United Nations Environmental Programme. Hertwich, Edgar G., et al. Online at http://www.unep.org/resourcepanel/Portals/24102/PDFs/PriorityProductsAndMaterials_Report.pdf. (Accessed 12 July 2012).

United Nations report on the Conference on Environment and Development, 1992.

United States Environmental Protection Agency. "Sustainable Materials Management." June 2009.

United States Department of Energy. "U.S. Energy Requirements for Aluminum Production: Historical Perspective, Theoretical Limits and Current Practices." 2007.

United States Environmental Protection Agency. "Tools for the Reduction and Assessment of Chemical and other Environmental Impacts (TRACI): User's Guide and System Documentation." June 2003.

United States Geological Survey. "Materials Flow and Sustainability." June 2008.

Usifer, Doug. "Scrap Metal Recycling: Expanding in a Recovering Environment." American Recycler, 2012. Online at http://www.americanrecycler.com/0512/1549scrap.shtml. Accessed 14th November, 2012.

Dr. Warhurst, Michael. "Overcoming the Barriers: Policies to Create a 'Real Recycling Society'." The Recycling Consultative Forum, Ireland, 2007. Online at http://www.environ.ie/en/Environment/Waste/ProducerResponsibilityObligations/RecyclingConsultativeForum/FileDownLoad,16411,en.pdf. Accessed 27 January, 2014.