Towards sustainable material usage: time-dependent evaluation of upgrading technologies for recycling

by

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Abstract

As consumption in the US grows, so does concern about sustainable materials usage. Increasing recycling is a key component within a broad arsenal of strategies for moving towards sustainable materials usage. There are many barriers to increasing recycling; one that is problematic is compositional uncertainty in the scrap stream. Repeated recycling compounds this problem through the accumulation of tramp elements in the material stream over time. Pertaining to the available operational and technological strategies that exist to mitigate accumulation, this thesis addresses the following questions: 1) How effective are these strategies at mitigating accumulation? 2) Under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams?

To answer these, a method was developed combining dynamic material flow analysis with optimal allocation of those materials into production portfolios using blending models. This methodology thus captured 1) the flow of EOL scraps, 2) how the economics of production are affected by changes in technology, and 3) a characterization of how recycling parameters influence accumulation in recycled streams. Using this methodology, optimal allocation was found to be an effective strategy for mitigating accumulation, for example, iron in the scrap stream was 69% less when compared to the value projected by conventional statistical methods.

Two upgrading technology cases were examined using the time-dependent methodology developed: shredding, sorting, and dismantling of aerospace scraps and fractional crystallization. Case results indicate that the time-dependent value of these technologies relies on whether or not the scrap stream is compositionally or availability constrained. These values were compared to analysis that does not consider repeated recycling (time-independent). Results show that undervaluing will occur in a regime where scrap availability is constrained and there is significant compositional accumulation occurring, a regime that may very well represent the reality faced by aluminum secondary producers in the US.

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Chapter 1. Introduction

1.1 Motivation to increase recycling

Consumption of materials in the United States as well as globally has risen exponentially over the last century (Figure 1). This growing usage requires increased production, which is often accompanied by a higher environmental burden in terms of increased energy usage, waste, and emissions. Issues such as growing materials scarcity, regulations, and the push for corporate responsibility put pressure on firms to begin to address creating a more sustainable materials market. Engineers, business leaders, and scientists must incorporate environmentally-aware decision–analysis to meet these pressures. One key materials selection opportunity with wide economic and environmental implications is the use of secondary (i.e. recycled), materials in production.

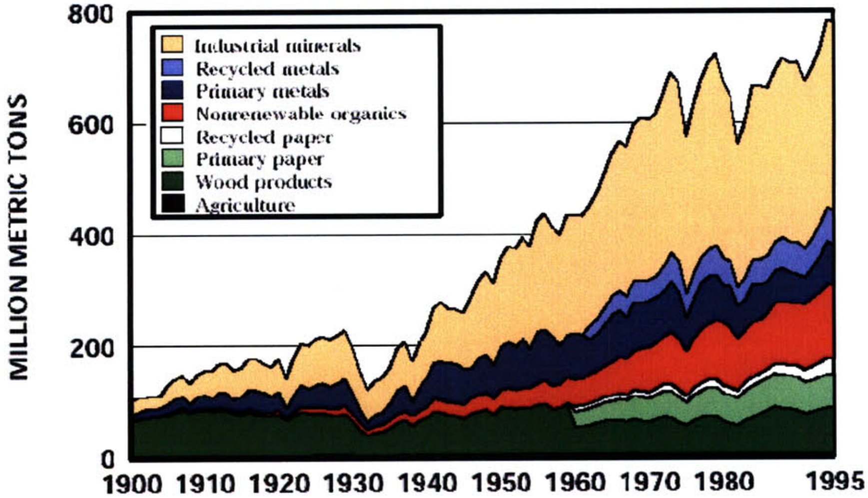


Figure 1. Consumption of materials in the United States in the last century, reproduced from (Matos and Wagner 1998)

Enabling the long term sustainable usage of materials will require a robust secondary recovery industry. Secondary recovery forestalls depletion of non-renewable resources and avoids the deleterious effects of extraction and winning (albeit by substituting some effects of its own)(Chapman and Roberts 1983). For most materials, the latter provides strong motivation for recycling as shown for several materials in Figure 2. For example, plastics, shown at the right hand side of the figure, require 1-2 times more energy for primary production compared to secondary production and savings of 55% for steel and copper to 81% for lead are realized by using secondary materials. For light metals, the motivation is particularly compelling; compared to other materials, aluminum production has one of the largest energy differences between primary and secondary production: 175 MJ/kg for primary compared to 10-20 MJ/kg for secondary(Keoleian, Kar et al. 1997). Aluminum also has a rapidly growing rate of consumption when compared to other metals with significant potential energy savings from using secondary materials (Figure 3). This combination motivates using aluminum as the case material of choice because increasing effective aluminum recycling has a potentially large impact. The methodology developed in this thesis can be generalized beyond aluminum and applied to other recycled material streams with little or no alteration.

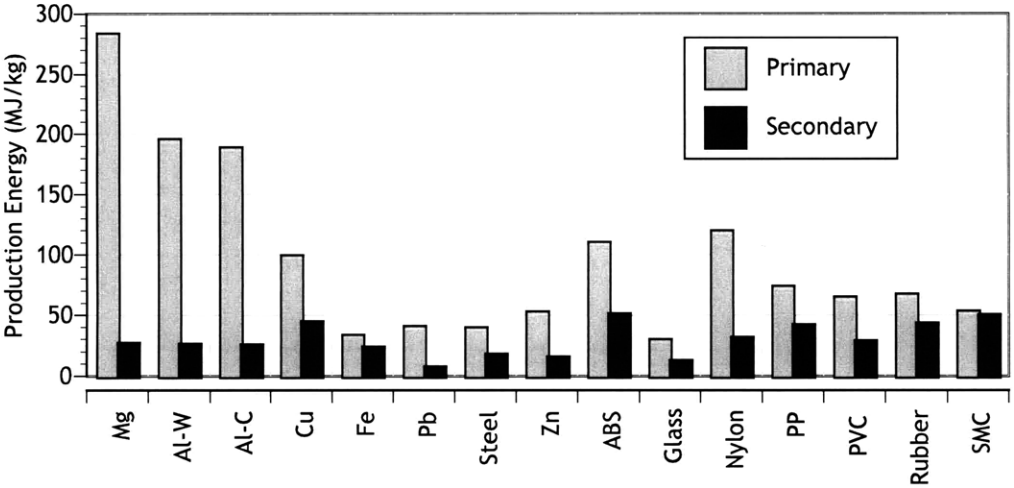


Figure 2. Primary and secondary production energy for a variety of materials(Keoleian, Kar et al. 1997)

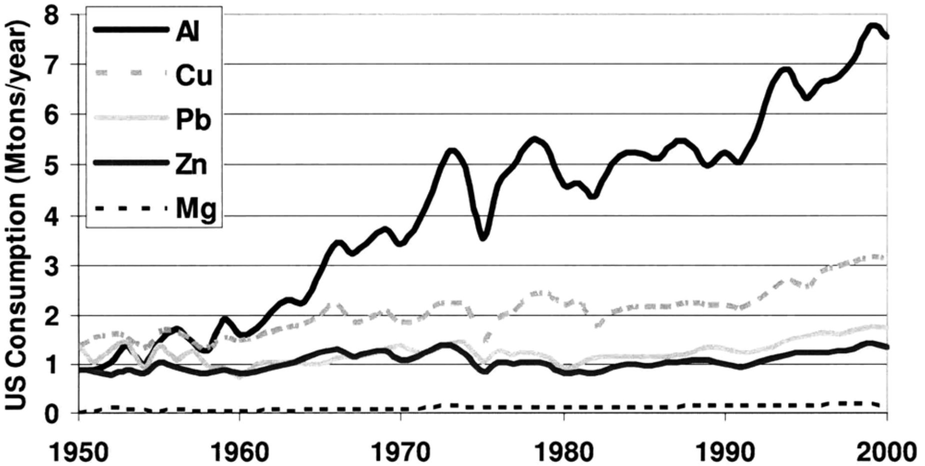
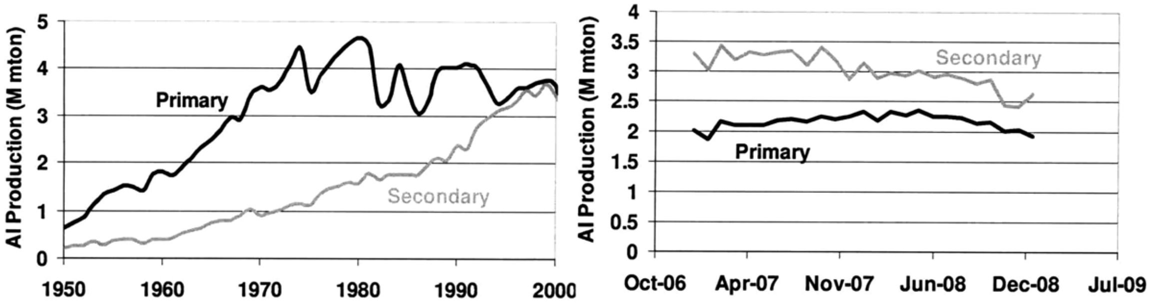


Figure 3. Apparent consumption in the United States for various metals from 1950-2000(Kelly and Matos 2006)

Fortunately, this self-same energy advantage creates a strong economic incentive for secondary production. In response to this, aluminum recycling is a rapidly growing business. In the US, over the last four decades, secondary aluminum production has risen from 178,000 metric tons per year to over 2,930,000 metric tons per year, a growth rate more rapid than any other major metal over the same period(Kelly and Matos 2006). Currently, the growth of secondary production has begun to outpace primary aluminum production (Figure 4A). The recent economic downturn highlights this behavior; Figure 4B shows that while total aluminum production decreased during 2007 and 2008 in the United States, secondary production was higher than primary.



A) B)

Figure 4. A) Primary and secondary production of aluminum in the US from 1950 – 2000, B) recent primary and secondary production(Kelly and Matos 2006)

Despite these large energy savings and the rise in secondary production, recycling is not necessarily increasing in the United States. Recycling rate is generally represented in one of two ways as shown in Equation (1.1), the key difference being whether the denominator is consumption or production. Another important distinction is the difference between "old" and "new" scrap. "Old" scrap is collected from discarded or end-of-life products while "new" scrap (also called "prompt") is generated during fabrication and manufacturing. While both types of recycling offset primary production, recycling end-of-life materials is considerably more compositionally challenging due to 1) the metal of interest being combined with other materials when made into a product, and 2) contamination from end-of-life processing.

$$\text{recycling rate} = \frac{\text{old + new scrap}}{\text{apparent consumption}} \quad \text{or} \quad \frac{\text{old + new scrap}}{\text{primary + secondary production}} \tag{1.1}$$

Aggregate recycling rates of most materials in the US hover below 50% with old scrap accounting for less than half of that figure. This is notable because while old scrap may be more challenging to collect and use, there is potentially much more end-of-life scrap available compared to prompt scrap; this end-of-life material is present in the products stored in use(Sullivan 2005). Also, the likelihood of prompt scrap being discarded or landfilled is very low while studies(IAI 2005) have found that at least 34% of available end-of-life products are currently not recycled. More troubling is the general stagnancy or decrease in these recycling rate figures over the last few years (Figure 5). For the case of aluminum, secondary production has tracked with increased consumption, so recycling rate hovers around 45% with old scrap accounting for 35% of that figure (Figure 6). To expand recycling, it is necessary to remove or reduce the disincentives to return, collect, and process secondary material (Wernick and Themelis 1998; Goodman, Kelly et al. May 20, 2005).

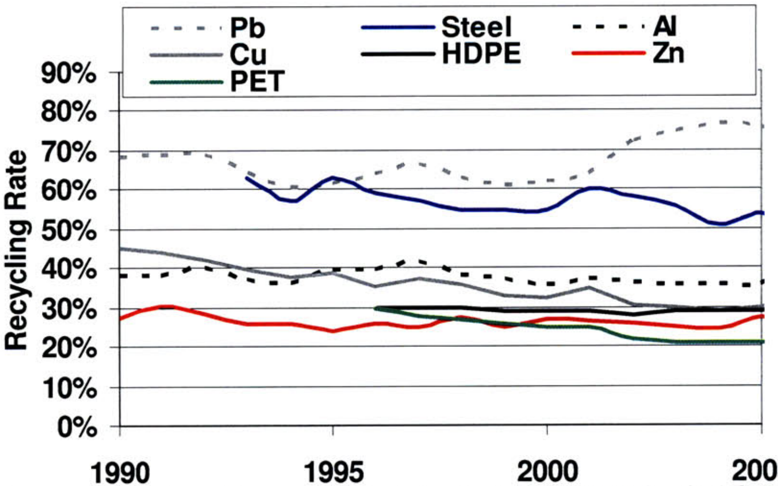


Figure 5. Aggregate recycling rates (old+new scrap/primary+ secondary production) for several materials in the United States from 1990-2005(Kelly, Buckingham et al. 2004)

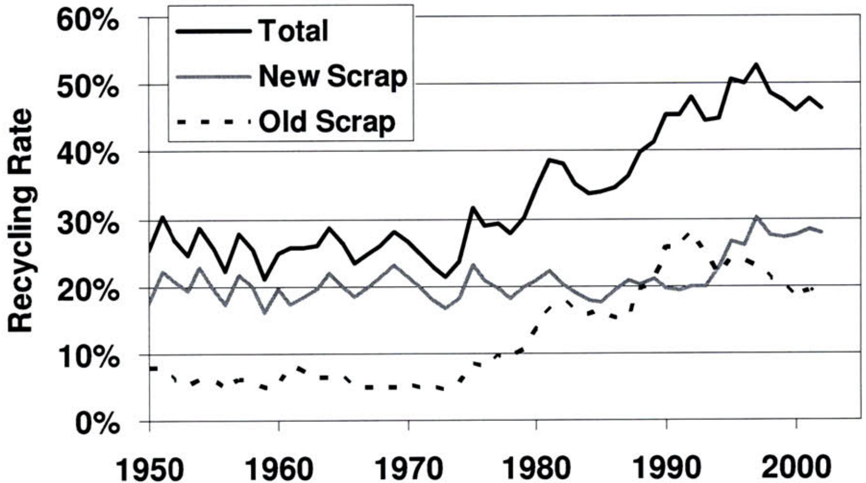


Figure 6. Recycling rate (1) old scrap, 2) new scrap, 3) old+new scrap/total consumption) for aluminum in the US from 1950-2003(Kelly and Matos 2006)

1.2 Barriers to increasing recycling: focus on uncertainty

There are a wide variety of barriers that prevent increased usage of recycled or scrap materials. Some of note in the literature include:

- limited participation by consumers(Watts, Jones et al. 1999; Morgan and Hughes 2006)
- inefficient regulations that do not properly incentivize participation (Kulshreshtha and Sarangi 2001; Porter 2002) or are unrealistic(Reuter, van Schaik et al. 2006)
- uncertain alloy demand(Li 2005; Gaustad, Li et al. 2006)
- uncertain scrap availability(Toto 2004)
- high cost of collection (Porter 2002; Calcott and Walls 2005)
- volatility of prices(Lee, Padmanabhan et al. 1997)

- uncertainty surrounding composition of scrap(Peterson 1999)
- low quality of recycled products(Vigeland 2001)
- lack of markets for some recycled products(Woodward 1997; Gesing 2004)

The role of sociological aspects should not be downplayed; factors that fuel participation (such as education, improved access, etc.) in recycling collection systems are an important cornerstone to increasing overall recycling rates, particularly for the case of aluminum(Watts, Jones et al. 1999; Das and Hughes 2006). Legislation can have a significant role in influencing the recycling rates of certain products. For example, in 2001 the recycling rate for beverage containers in the United States was approximately 40%. States with deposits or bottle bills had significantly higher recycling rates of 78% while states without averaged a 23% recycling rate(McCarthy 1993; Porter 2002). While the role of consumer and government stakeholders within the aluminum recycling system will be discussed further in section 9.1.3, the work in this thesis will focus on the barriers faced by secondary producers, and in particular, the many forms of uncertainty surrounding secondary materials that make increased scrap utilization challenging. The following sections will discuss some of the sources of these uncertainties.

Uncertainty is a reality that confronts all businesses; materials producers are no exception. When business plans do not accommodate actual operating conditions, businesses are left with the negative economic impact of inefficient use of capital, materials, or potential market consumption. A significant set of economic disincentives to increased secondary materials use emerge due to the various types of operational uncertainty that confront secondary metal processors (Peterson 1999; Khoei, Masters et al. 2002; Rong and Lahdelma 2006). In particular, depending on where one is in the production chain, sources of uncertainty include capricious demand, unstable availability of raw materials (particularly scrap materials), the price of materials, and the variation in composition of those raw materials. These uncertainties have the largest adverse effect on those furthest from the customer, e.g. materials producers, due to the feedback mechanisms inherent to typical market-based supply-chains (Lee, Padmanabhan et al. 1997).

Uncertainties will affect the decisions that secondary producers must make, specifically, their *blending, or batch-planning* decisions. Producers are faced with a wide selection of raw materials including primary, alloying elements, and secondary materials; these feedstock materials are used to manufacture a variety of finished alloys. Producers must take into consideration demand, availability, price, and composition when making the decision of what mix or blend of these materials they will select to create their production portfolio or batch-plan. Despite real uncertainties in each of these parameters, these business-critical decisions must be made on a daily basis.

1.2.1 Uncertainty surrounding demand and availability

An appreciation of uncertainty in demand and availability pertaining to the aluminum industry can be gained by examining Figure 7 and Figure 8. Figure 7 shows the year to year change in apparent aluminum consumption in the United States over several decades, an illustration of the volatility of finished alloy demand. Scrap availability shows similar volatility (Figure 8), especially over the past few decades considering exports to rapidly industrializing countries such as China and Brazil.

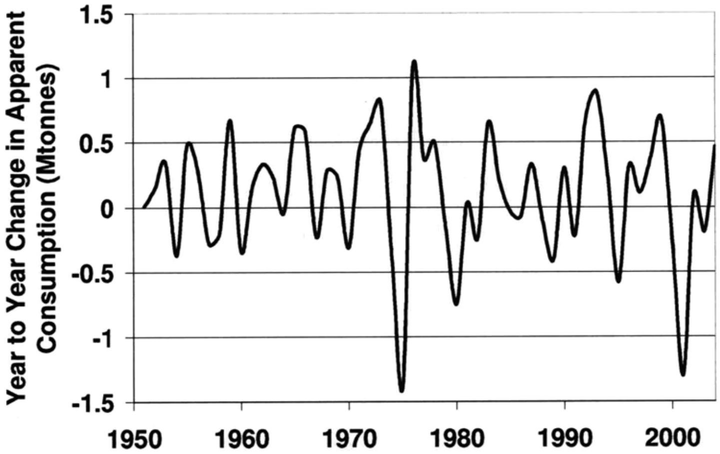


Figure 7. Year to year change in apparent aluminum consumption in the US from 1950-2004(Kelly, Buckingham et al. 2004)

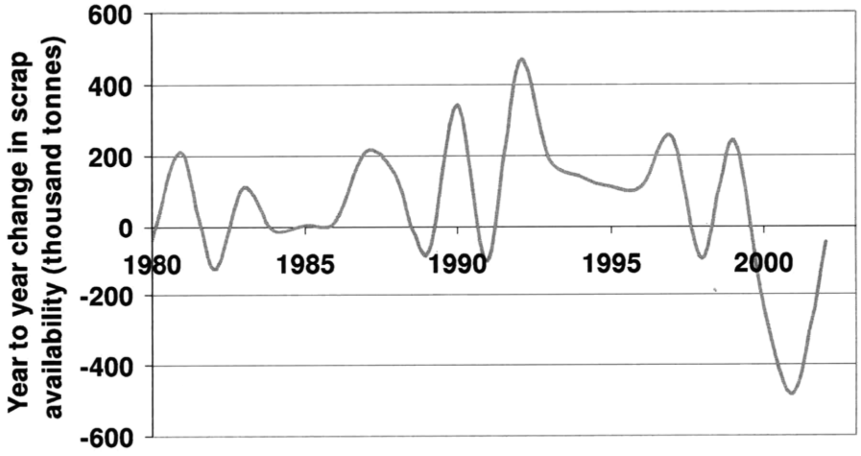
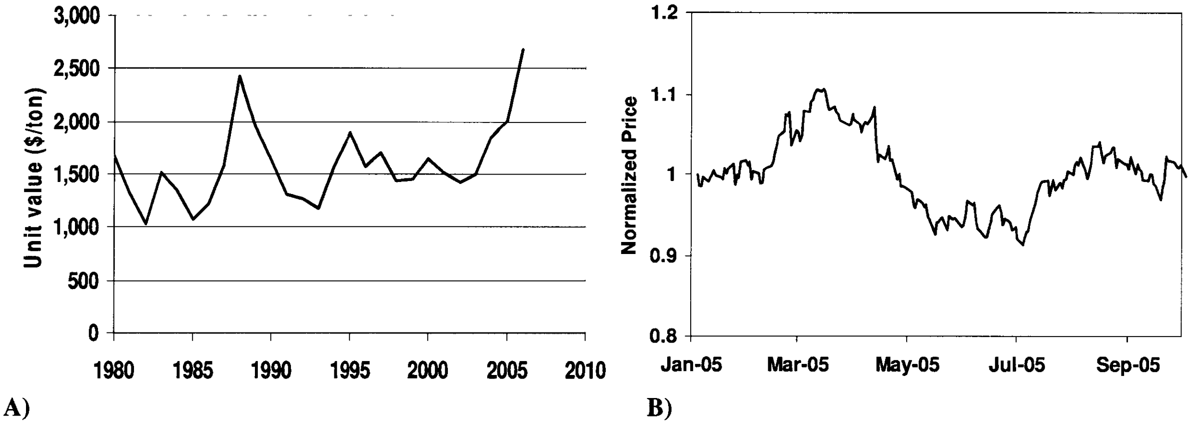


Figure 8. Year to year change in total scrap generated (new + old) in the US from 1980 – 2003 in thousands of metric tonnes(Kelly and Matos 2006)

1.2.2 Uncertainty in price

Although the overall price trend (or unit value) of primary over the last four decades is one which is clearly favorable to all aluminum producers[1], the significant variance of price (up to 48% over this time frame) represents not only a direct form of operating uncertainty, but also belies the underlying swings in demand which confront operational decision-makers (Figure 9A). These values, because they have been averaged over the year, do not fully capture the true volatility of price. Figure 9B shows the normalized London Metals Exchange price for primary aluminum over several months in 2005. These values give an indication of the variance present in day-to-day pricing.

Scrap shows even larger volatility in price as shown in Figure 10. This is due in part to geographic/regional price differences for different types of scrap materials; the American metals market (AMM) tracks scrap prices for fourteen US and two Canadian[2] cities with differences as large as 46% between them for the same scrap and time period(Market 2006). There are a variety of reasons for this regional price difference, for example, scrap dealers near cities potentially have larger supply of UBC's (used beverage cans) and therefore can offer lower prices; scrap dealers in the Midwest have access to large amounts of automotive-heavy mixed scraps and therefore lower prices on those types. Aluminum siding may be in large supply, and therefore have a lower price, in areas of the country where expansion and development are taking place (the southwest and Florida for example). Such large price differences (e.g. approximately 47% difference between the maximum and minimum prices for auto wheels over a period of two years) over such a short period of time can lead to significantly different decisions over which scraps to use in secondary production.



A) B)

Figure 9. A) Unit value of aluminum in the US from 1980-2006(Kelly and Matos 2006), B) Normalized London Metals Exchange daily cash settlement prices for Jan – Sept 2005 (Jan. 4, 2005 = 1)

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[1] Neglecting the current economic downturn which has resulted in significantly lower metal prices

[2] US cities: Atlanta, Boston, Buffalo, Chicago, Cincinnati, Cleveland, Detroit, Houston, Los Angeles, New York, Philadelphia, Pittsburgh, San Francisco, and St. Louis; Canadian: Montreal and Toronto

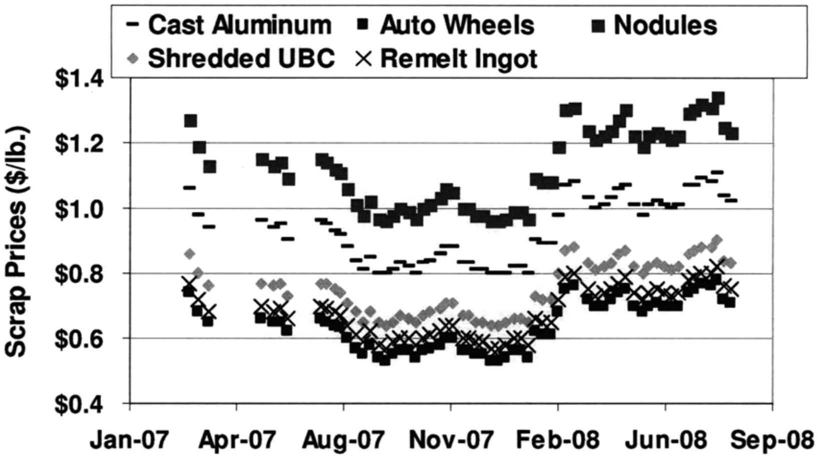

Figure 10. Weekly average scrap prices in the United States over two year period from multiple dealers(2007)

1.2.3 Compositional uncertainty

Elemental considerations for scrap have been identified as the most significant source of uncertainty in the production process (Liu 2003; Rong and Lahdelma 2006). To provide an indication of the scope of this form of uncertainty, Figure 11 shows mean composition and standard deviation of several alloying elements within recycled aluminum siding sampled over a period of one year; one can see the wide range in both mean and variance. For elements like magnesium and zinc in painted siding, the mean is expected to be quite low; therefore the extremely large standard deviation from the mean indicates a coefficient of variation[3] well over 1,000%. Considering the many types of recycled materials secondary producers use multiplied by the dozens of relevant compositional elements, it is clear that compositional uncertainty makes it difficult to meet quality specifications and, thereby, creates a strong disincentive to usage of recycled materials.

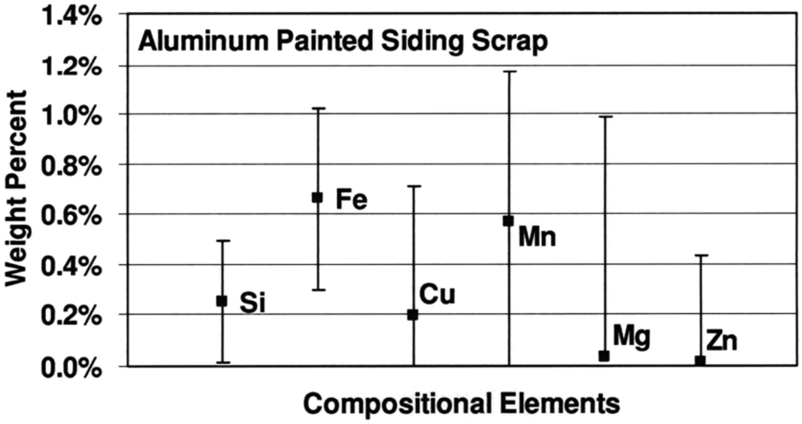

Figure 11. Compositional uncertainty (mean and standard deviation of various elements) in scrap aluminum siding sampled over the course of a year (Peterson 1999)

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[3] Coefficient of variation is equal to the standard deviation normalized by the mean

Many alloying elements are present within aluminum because they have been purposefully added during processing in order to achieve certain properties. Table I shows the Aluminum Association (AA) alloy family designations for both wrought and cast products which describe the major elements present in typical aluminum alloys. The AA also provides industry specifications for aluminum alloys; each element within the alloy must fall within the range provided by these minimum and maximum specifications. Because a window exists, different producers may have different amounts of alloying elements in the same alloy. This is one of the sources of uncertainty pertaining to the composition of recycled materials.

Table I. Aluminum Association alloy family designations showing major alloying elements for each series

	Wrought	Cast
Pure Al 99% or higher	1XXX	1XX
Major alloy elements:		
Copper	2XXX	2XX
Manganese	3XXX	
Silicon	4XXX	4XX
Magnesium	5XXX	5XX
Magnesium & Silicon	6XXX	
Zinc	7XXX	7XX
Other & Specialized	8XXX	9XX
Tin		8XX
Si + Cu + Mg		3XX

To illustrate how this can be problematic consider an example. Company A and Company B are aluminum manufacturers each producing alloy 6061, a highly produced common automotive sheet alloy. The AA provides guidelines as to the minimum and maximum amounts of several elements as shown in Table II. "Other each" is a maximum for any other individual alloying element not listed and "other total" is a maximum for the total of these other elements. Company A has a customer whose application allows or requires most of the alloying elements to be near the maximum specification while Company B has a customer that requires the alloy to be produced to the minimum specification. Although both the resulting alloys are designated to be 6061 by the AA, one can see that their composition is significantly different, resulting in a total aluminum content difference of nearly 3% (Table III). Also, while Company A could use recycled 6061 from Company B; the reverse would not be possible.

Table II. AA specification for alloy 6061 (wt. %)

	Min	Max
Si	0.4	0.8
Fe	0	0.7
Cu	0.15	0.4
Mn	0	0.15
Mg	0.8	1.2
Cr	0.04	0.35
Zn	0	0.25
Ti	0	0.15
Other Each	0	0.05
Other Total	0	0.15

Table III. Average composition for alloy 6061 for company A and company B (wt. %)

	Co. A	Co. B
Si	0.8	0.4
Fe	0.7	0
Cu	0.4	0.15
Mn	0.15	0
Mg	1.2	0.8
Cr	0.35	0.04
Zn	0.25	0
Ti	0.15	0
Ni	0.05	0
Ga	0.05	0
V	0.05	0
Total AE	4.15	1.39
Al Content	95.85	98.61

Besides these desired alloying elements that are added purposefully, recycled materials will often include high levels of unwanted, or "tramp" elements. These elements are present due to a variety of sources such as material joining that occurs in product manufacture or end-of-life processing that results in pick-up; these sources will be discussed further in the next section. Many of these elements will increase or *accumulate* with repeated recycling of products(Kim, Kim et al. 1997; Daigo, Fujimaki et al. 2004; Hatayama, Yamada et al. 2007), hence the strong influence of compositional uncertainty on secondary production decisions(Gaustad, Li et al. 2007; Rong and Lahdelma 2008). This accumulation is a *time-dependent* process based on this repeated recycling over multiple scrap generations.

1.2.4 Accumulation

A growing number of studies and literature would suggest that accumulation of unwanted elements is a growing problem, in all recycled material streams. Table IV shows a brief literature review of various recycled material streams and their problematic accumulated elements. One can see that aluminum has a significant list. Many of these elements, for example, iron and silicon in the case of aluminum, are accumulated due to end-of-life processing such as shredding. Much literature exists that pinpoints problematic elements in aluminum for various negative impacts on properties including: magnesium, nickel, zinc, copper, lead, chromium, vanadium, gallium, manganese and silicon.

Table IV. Possible tramp elements that increase with recycling

Material	Tramp Elements				
Steel	Ni, Cr, Sn(Noro, Takeuchi et al. 1997; Menad 1999)	Cu(Noro, Takeuchi et al. 1997; Menad 1999; Cho, Fan et al. 2004; Daigo, Fujimaki et al. 2004)	Zn(Noro, Takeuchi et al. 1997)		
Plastics	Cd				
Aluminum	Mg, Ni, Zn, Pb, Cr(Lundqvist, Andersson et al. 2004)	Fe(Kim, Kim et al. 1997; Lundqvist, Andersson et al. 2004; Das 2006)	Cu(Kim, Kim et al. 1997; Lundqvist, Andersson et al. 2004)	V, Mn(Kim, Kim et al. 1997)	Si(Kim, Kim et al. 1997; Das 2006)
Brass	Pb				
Copper	Fe, Pb, Ni, Cr, Sb, Bi, Se, Te(Lundqvist, Andersson et al. 2004)				
Glass	Al, SiC, C, Chromite, Carborundum(Lundqvist, Andersson et al. 2004)				
Cast Iron	Mn, Ni, Mo, Zn, Co(Anigstein, Thurber et al. 2001)				

Studies on recyclability and disassembly(Johnson and Wang 1998; Castro, Remmerswaal et al. 2004; Oyasato and Kobayashi 2006) point out the challenges in tracking and mitigating impurity element accumulation in recycled materials. One study in particular attempts to overcome this challenge by developing general removability rules for recycled metals as shown in Table V. An "A" designates an element in the recycled metal stream that is either removable or whose addition is usable as an alloying element, a "B" designates an element that is difficult to remove but does not accumulate at a high level, while a "C" designates the most problematic elements – those that are difficult to remove and accumulate at a high rate with repeated recycling. One can see that aluminum (highlighted in yellow and bold) has many C designations when compared to other recycled metal streams.

Table V. Accumulation and removability of impurities in metals, reproduced from (Oyasato and Kobayashi 2006) "A" = removable or usable as an alloying element, "B" = removal difficult, does not accumulate, "C"= difficult to remove and rapid accumulation

		Impurities																		
		Fe	Cu	Al	Zn	Pb	Cr	Ni	Co	Mo	Sn	As	Sb	Bi	Mn	Ti	Si	Mg	Li	Cd
Metals	Fe		C		A	A	B	B	B	B	C	B	B	B		B				B
	Cu	A		A	A	A	A	C	A		A			C			A			
	Al	**C**	**C**		**C**	**C**					**C**				**C**	**C**	**C**	**A**	**A**	
	Zn	A		A		B							B				A			
	Pb		A								A	A	A							
	Cr	B																		
	Ni	B																		
	Co	B																		
	Mo	B																		
	Sn																			
	As																			
	Sb																			
	Bi																			
	Mn																			
	Ti	A	A	A				A	A											
	Si																			
	Mg	C	C	C	A		C	C												
	Li																			
	Cd																			

Highly recycled aluminum products can have a variety of compositional accumulation issues stemming from mechanisms beyond alloying element additions. Figure 12 shows the percentage for old scrap consumed in the United States and Canada in 2005 broken down by scrap type. The dominant scrap types are used beverage cans (UBC's), castings, shredded automotives, and other wrought extrusions. Table VI outlines some of the major problematic alloying elements and other quality issues within each of these scrap streams.

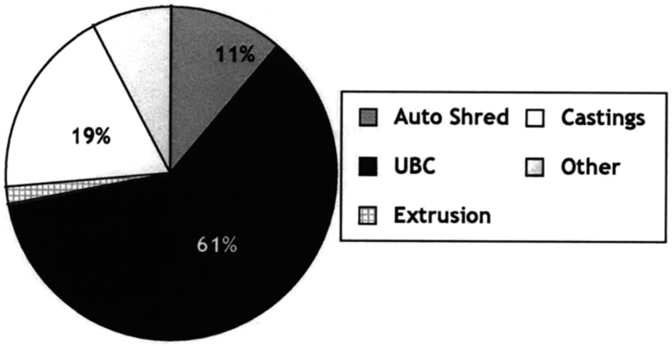

Figure 12 Percentages of old scrap consumed (total 1,154,000 metric tonnes) in the United States and Canada in 2005(Kelly and Matos 2006)

Table VI. Major scrap streams, their main quality issues and the mechanism for accumulation

Scrap Stream	Quality problems	Reason	References
UBC	paint	coatings/labels on cans	(Das and Hughes 2006)
	plastics	caps and co-mingled beverage containers	(Green 2007)
Castings	Si	high allowable specification for Si	(Gesing 2001; Das 2006)
Auto Shred	Fe	pick-up from shredding and handling machinery; many steel pieces remain co-mingled	(Gesing 2001; Gesing 2004)
	Cu	automobile radiators have high Cu content	(Brahmst 2006; Ruhrberg 2006)
	plastics	high plastic content in cars	(Nourreddine 2007)
	Mg	other light-weight components	(Neff 1991)
Extrusions	Fe	pick-up from cutting and stamping machinery	(Xiao and Reuter 2002)
Other	alumina inclusions	present due to oxidation	(Veasey, Wilson et al. 1993; Roy, Utigard et al. 1998)

The previous sections have provided motivation to increase recycling while outlining the challenges in doing so, specifically emphasizing uncertainties in demand, availability, price and composition. Compositional barriers, particularly accumulation of alloying elements in the recycled scrap stream, are one of the most prevalent and problematic. These barriers necessitate a materials engineer to address; these facts have motivated the focus of this work. This thesis provides strategies for addressing these barriers by developing a methodology to examine the value of various operational and technological solutions. It is first useful to understand what some of those operational and technologies strategies may encompass.

1.3 Strategies for managing barriers to recycling

1.3.1 Operational

Previous work by the author(Gaustad, Li et al. 2007; Gaustad 2009) has examined two specific operational strategies for increasing recycling: 1) efficient blending plans and 2) the redesign of alloys to accommodate more scrap. Both blending and redesign typically proceed by expensive trial-and-error; this work showed that mathematical tools which explicitly consider compositional uncertainty have the capability to reduce and sometimes eliminate this rework. Specifically, results from the framework developed suggested batch plans that increased scrap utilization by nearly 30% over batch plans derived by conventional methods as well as provided a direct mechanism to control expected batch error rates. For the cases exploring alloy design, the framework was shown to be a systematic method to (1) evaluate an alloy's ability to accommodate recycled materials (scrap) in its production portfolio and (2) proactively identify the most effective alloy modification strategies that can drive increased potential scrap use.

There are a variety of additional operational solutions that firms employ to deal with the negative impact on recycling due to accumulation of undesired elements. Dilution with primary is the most common; this has a negative impact on recycling as the required dilution results in a compositionally-determined cap to recycling rates. "Down-cycling", where materials are recycled into lower value products, is another common method of dealing with highly contaminated secondary materials; this enables higher usage of recycled materials but negatively effects recycling economics. A specific example of down-cycling is when wrought scrap is used in cast products due to their ability to accommodate higher silicon contamination.

1.3.2 Technological

Other current processing solutions to the accumulation problem are more technological in nature. These might include dismantling of end-of-life products, spectrographic or magnetic sorting of shredded scrap, and "filtration" technologies that attempt to remove elements in the melt such as fractional crystallization and vacuum distillation. A variety of other technologies exist that are still in the early stages of research and development. These technologies will be more fully described in chapter 4. Although, qualitatively it is clear that such technologies could be useful, it is not clear that they would be economic and/or efficient. Each strategy will have a trade-off between cost and scrap utilization, as estimated schematically in Figure 13; understanding this trade-off is critical to determining the value of these potential solutions. Therefore, this work aims to develop a set of analytical tools to quantify the potential value of scrap "upgrading" technologies, including filtration, segregation, and sorting technologies.

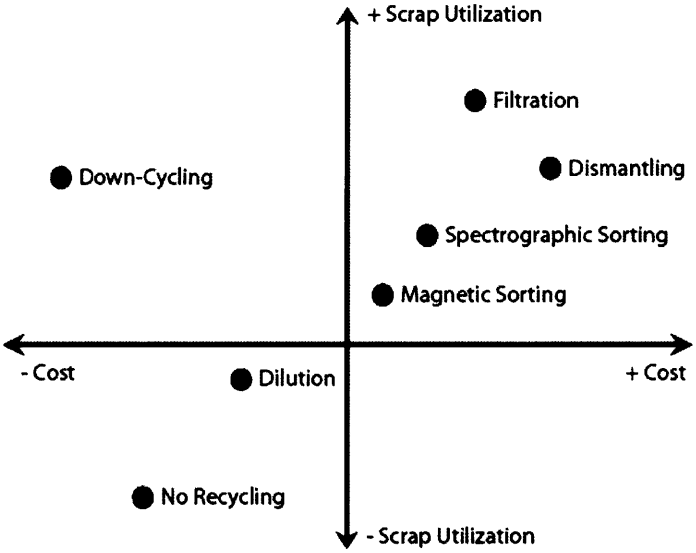

Figure 13. The cost and scrap utilization trade-offs of various strategies for dealing with compositional accumulation

Compositional uncertainty presents a major barrier to the increased usage of recycled materials; repeated recycling compounds this problem through the accumulation of tramp elements in the recycled material stream. To evaluate these potential operational and technological strategies to mitigating accumulation, a long-term, time-dependent framing of the stakeholders and decision makers within the recycling system must be provided. This framing and an outline of the thesis is provided in the next section.

1.4 Thesis description - a framework for evaluating upgrading technologies

This thesis will address the following questions:
1) How effective are operational or technological strategies at mitigating accumulation?
2) Under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams?

In order to answer these, first the tools to evaluate the economic and environmental impact of upgrading for a single generation will be developed. Then, to consider the value in a time-dependent, multi-generation, open loop recycling system, the material flows of aluminum scrap must be modeled. Figure 14 illustrates many of the key material flows that must be captured. The secondary producer, highlighted in yellow, is a key decision-maker deciding what mix of materials (primary aluminum, alloying elements, as well as prompt and end-of-life scrap) to choose in order to produce the alloys demanded. Primary aluminum and alloying elements will come from primary production, the upper left box. Because the composition of primary aluminum and alloying elements are well-known, price becomes the main leverage point for decisions regarding their use.

To accurately inform the decision-making at the secondary producer, it is necessary to capture the flow of materials from both prompt and EOL scrap. Both prompt scrap and EOL will have changes in composition and price as leverage points although it is assumed that prompt will only have slight changes in composition compared to EOL scraps. Prompt scrap comes directly from fabrication; end-of-life scrap has a much more complicated mechanism of return. Its composition, availability, and price will depend upon the lifetime of the product, collection rates, losses to land-filling, exports, and dissipation, and the way it is processed. Whether or not to use upgrading technologies on either of these scrap streams is a decision the producer must make.

Traditional analyses of scrap flows have relied upon market-wide statistical metrics that tend to mask fine technical structures that might offer desired insights into the management of compositional drift. Previous work looking at decision-making at the secondary producer level has neglected the effects of accumulation in a multi-generation closed loop recycling system. A summary of this previous work and an analysis of its gaps will be discussed in more detail in the next section. This thesis will attempt to overcome these gaps by capturing both of these aspects of aluminum recycling, the agency of the decision maker and the time-dependency of composition.

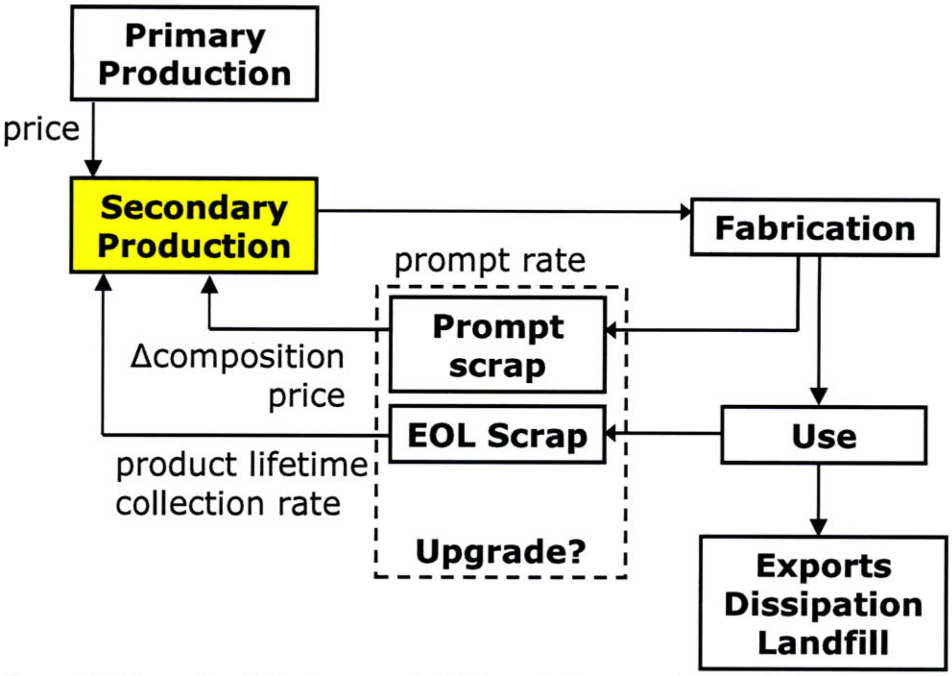

Figure 14. Schematic of aluminum material flows in the secondary market

The sequence of this document will flow as follows. Chapter 2 will outline previous work that has looked at 1) the materials flow of end-of-life scraps, 2) accumulation of tramp elements in recycled material streams, and 3) optimizing scrap blending decisions. This chapter will summarize the gaps in this body of work and outline the contribution of this thesis in that area. Chapter 3 will outline the methods that will be used to populate the methodology described above. Chapter 4 discusses various upgrading technologies for recycled aluminum that are available outlining their prevalence and capabilities. Chapter 5 will examine the results of two case studies evaluating the value of fractional crystallization and sorting upgrading technologies. Major factors influencing the value of these technologies will be discussed. Chapter 6 shows which parameters must be characterized in order to extend to a time-dependent dynamic analysis. Chapter 7 uses the methodology developed in 6 to show the time-dependent value of the two upgrading technologies examined in 5. Chapter 8 provides a discussion and summary of the contribution of this thesis while chapter 9 outlines the limitations encountered and resulting future work.

Effective operational strategies for mitigating accumulation were found to include optimal allocation of scrap materials within batch planning. This is one of the reasons why developing a methodology that considers both materials flows *and* blending decisions is a critical contribution. Considering the wide variety of technological strategies, or upgrading work, it was found that a tool for valuation is essential. This work has found that a time-dependent multiple generation evaluation of upgrading technologies may differ significantly from a time-independent snapshot evaluation. This difference will depend heavily on the factors or leverage points outlined in Figure 14.

Chapter 2. Literature review and gap analysis

Exploring issues of mitigating compositional accumulation will require an understanding of 1) the flow of end-of-life scrap materials, 2) a method to evaluate how the economics of production are effected by changes in technology, and 3) a characterization of how recycling parameters influence accumulation in recycled streams. Each of these topics has been explored previously and each has a rich set of literature. This chapter discusses the relevant previous work in each of these areas as well as any gaps that exist.

2.1 General Material Flow Analysis (MFA)[4]

In order to attain a sustainable materials market, it is important to understand the relative magnitude of the flows within it. Capturing the flow of dynamic materials markets is quite complex and a large body of work is devoted to material flow analysis (MFA). A majority of the research conducting MFA typically focus on high volume, value, or toxicity materials(Graedel, Harper et al. 2006). As such, aluminum is often neglected in favor of materials such as iron and steel(Muller, Wang et al. 2006; Wang, Muller et al. 2007), pulp and paper(Ruth and Harrington 1998), and concrete(Kelly 1996) (high volume), copper, platinum, silver(Johnson, Jirikowic et al. 2005), and gold(high value), and cadmium(Hawkins, Matthews et al. 2006), cobalt, and lead(Tukker, Buist et al. 2006) (high toxicity).

At the highest level, the International Aluminum Institute (IAI) has captured the global flow of aluminum material for several years using a life cycle inventory (LCI) analysis(IAI 2005). This LCI characterizes the amount of aluminum recycled as old scrap, traded new scrap, and fabricator scrap as well as estimates the total products in use since 1888. This study shows that for 2003, a global recycling rate of 50.5% was achieved (recycled aluminum/recycled + primary aluminum consumed) although only 22.2% of that figure is from end-of-life scrap (11.2% overall). The LCI is useful in tracking gross flows as well as many environmental impacts such as alumina and primary production, greenhouse gas and perfluorocarbon (PFC) emissions, energy required for electrolysis, fluoride consumption and emissions for the aluminum industry as a whole. However, detail on the flows broken down by product/sector is not captured and 23% of

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[4] MFA alone may not capture the environmental impact associated with material use – two other categories of work that will not be covered in this thesis include ecological footprint analysis (including LCA) and thermodynamic analysis (exergy accounting) Fiksel, J. (2006). "A framework for sustainable materials management." Journal of Materials **58**(8): 15-22.

aluminum leaving stocks in use is unaccounted for (either to land-filling, undocumented recycling or reuse, or dissipative uses). This information is important for quantifying the quality of the recycled aluminum and not just its total amount.

The key gap in the IAI study is not treating scrap materials in detail, especially end-of-life aluminum scrap. When considering end-of-life recycled products, the complexities involved grow quite rapidly. Figure 15 shows how the aluminum market is divided between various end-use products in the United States with transportation, containers and packaging, and construction making up the top three categories (75% of total products in 2003)(Kelly and Matos 2006). The wide range in lifetimes for these products creates complexities in determining the availability and composition of the returning aluminum scrap stream. The vast majority of scrap in the containers and packaging category are used beverage cans which can have lifetimes as short as 60 days(Kelly 2008). In contrast, the lifetime for aluminum used in construction applications (siding for houses, roofing, etc.) can be decades. Automobiles which make up the majority of the transportation use sector, fall in the middle of these ranges with average lifetimes exceeding 15 years(Davis and Diegel 2002). The wide range in lifetimes, varying quantities of recycled products, and variety in collection and recycling processes make projecting future availability quite complex.

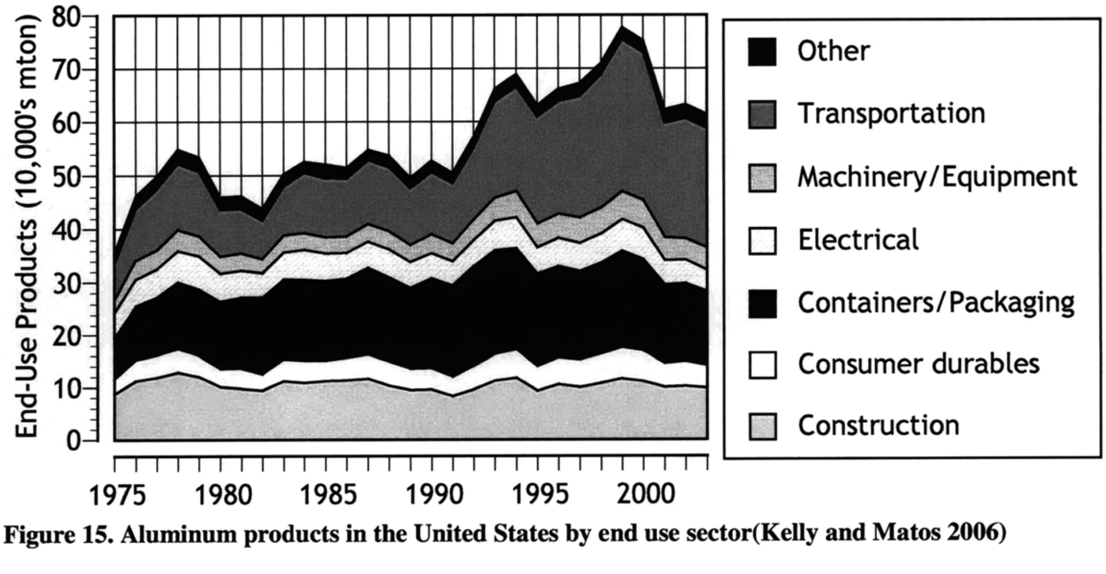
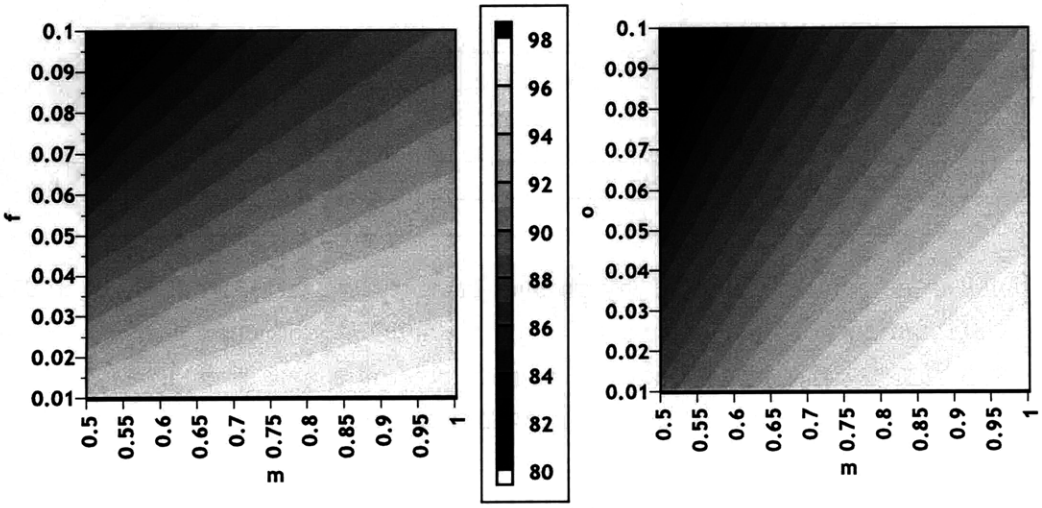


Figure 15. Aluminum products in the United States by end use sector(Kelly and Matos 2006)

One body of work(Boin and Bertram 2005) has begun to more accurately characterize the flow of manufacturing (prompt) and end-of-life aluminum scrap. This work conducts a mass balance for the fifteen European Union states from 1995 to 2004. Because there is little ore mining occurring in Europe, recycled aluminum makes up a large portion of production and therefore needs to be well characterized. The focus of this work is on the furnace-specific melting step for refiners and remelters. As defined for this study, a refiner produces castings and aluminum "deox" for purifying steel melts while a remelter produces wrought alloys; both use a large portion of scrap (both prompt and end-of-life) in their production portfolios. The metal yield and recovery are estimated according to the amount of scrap collected and characteristics of the scrap types according to Equation (2.1) where *o*= oxidized metal in the scrap, *m*=aluminum fraction in the, *f*=fraction of foreign materials in the scrap, and 1.89 is the stoichiometric conversion factor for aluminum metal into its oxide.

$$\text{Al metal} = \frac{\text{Scrap collected}}{\left[\dfrac{m}{m+\dfrac{o}{1.89}}+\dfrac{o}{m+\dfrac{o}{1.89}}+\dfrac{f}{m+o}*\left(\dfrac{m}{m+\dfrac{o}{1.89}}+\dfrac{o}{m+\dfrac{o}{1.89}}\right)\right]} \tag{2.1}$$

The effect of these parameters on the metal yield are shown in Figure 16; drosses, skimmings, and turnings will typically have *m* values around 0.5, cleaner scraps, such as castings and used beverage cans would typically be around 0.85, and wire and cable has some of the highest metal content with *m* values around 0.98 according to European Union scrap standards(2003). Values of *f* and *o* were varied between 0 and 0.10. As one would expect, the combination of high metal content value and low foreign and oxidized materials results in the highest recovery of pure aluminum metal.



A) B)

Figure 16. The effect of metal in scrap (m) and A) fraction of foreign materials present in the scrap (f) or B) fraction of oxidized metal in scrap (o), on the amount of aluminum metal yielded (A-contours) assuming 100 lbs. of scrap. Created using Equation(2.1) from (Boin and Bertram 2005)

This work concludes that the European Union has a remarkably high metal recovery rate of 98%. The authors caution that these results are subject to much uncertainty surrounding the lifetimes of recycled products and the collection of end-of-life scrap. They also state that tracking these scraps on the compositional level would be quite difficult as their resulting co-mingled compositions are generally unknown.

A group at Alcoa(Bruggink 2000; Martchek 2000; Martchek 2006; Martchek 2007) has also addressed the lack of detail about prompt and end-of-life scraps in current material flow analysis by examining the flows of aluminum in the United States with a life cycle inventory model. This LCI focuses on expanding details surrounding the collection, yield, and breakdown of end-of-life scrap materials. Estimates on product life, recycling rates, and metal recovery were made and are shown in Table VII. The model's predicted scrap collected agrees fairly well with reported values for old scrap between 1985 and 1998, however, does not agree as well for new scrap. Uncertainty surrounding collection and prompt scrap rates may fuel this difference but more likely is the uncertainty in production forecasts.

Table VII. Estimated lifetimes, recycling rates, and metal recovery by category from (Bruggink 2000)

Market	Lifetime (yr)	Recycling Rate	Metal Recovery
Building & Construction	40	15%	85%
Transportation-Aerospace	30	30%	90%
Trans-Auto & Light Truck	13	80%	90%
Trans-Trucks, Buses, Trailers	20	70%	90%
Trans-Rail	30	70%	90%
Trans-Other	20	70%	90%
Consumer Durables	15	20%	90%
Electrical	35	10%	90%
Machinery & Equipment	25	15%	90%
Containers & Packaging ex Foil	1	25-60%	90%
Containers & Packaging Foil	1	2%	80%
Other	15	20%	90%

Specifically, the demand forecasts by product category are taken from (King 1997); actual USGS production on average and for some individual production years are shown in Table VIII for comparison. One can see agreement on annual growth rate for some categories; however, individual annual growth rates fluctuate significantly. Some forecasts are also quite different even in aggregate, such as containers and packaging. This could significantly affect the model as used beverage cans, a majority of old scrap collected, fall in this category. Additionally, the forecasts assume an average total growth rate of 1.9% while the actual values show an increase of only 0.1%. Regardless of these differences, this work's contribution makes it possible to look at changes in environmental impact of different recycling scenarios which would not otherwise be possible in MFA work lacking details on scrap break-down. However, this work does not project compositional impacts of these scenarios or examine the effect on producers.

Table VIII. Projected(King 1997) and actual(Kelly, Buckingham et al. 2004) annual growth rate in the United States of aluminum products by category; projected is a 1995-2015 forecast and actual is the average for 1995-2003 with individual year growth rates shown to the right

	Proj.	Actual	1996	1997	1998	1999	2000	2001	2002	2003
Containers & packaging	2.5%	-2.6%	-1.7%	-2.9%	3.6%	5.2%	-5.5%	-13.3%	-1.3%	-4.7%
Building & construction	1.3%	1.0%	13.4%	-4.8%	7.0%	8.4%	-4.3%	-9.9%	2.0%	-3.8%
Transportation	2.5%	2.0%	5.5%	7.6%	10.2%	14.1%	-2.8%	-22.8%	5.2%	-0.9%
Electrical	-0.1%	-2.0%	6.4%	0.8%	1.9%	7.7%	0.2%	-22.2%	-3.7%	-7.2%
Consumer durables	1.8%	-0.6%	9.9%	0.8%	6.1%	7.9%	-2.2%	-22.5%	4.2%	-8.6%
Machinery & equipment	-0.1%	-0.3%	3.9%	4.0%	2.6%	8.3%	-0.4%	-17.5%	-5.8%	2.5%
Other	1.4%	2.9%	7.5%	5.7%	-13.6%	10.0%	-2.2%	9.3%	5.7%	0.4%

2.2 Dynamic MFA: Population balance and residence time models

Another set of models used to project the availability of recycled scrap streams are residence time models. In these, Markov chain modeling provides estimates of the average number of times of use of an element by using transition matrices of products and their lifecycle stage. This methodology, developed by a research group at the University of Tokyo(Daigo, Matsuno et al. 2005; Yamada, Daigo et al. 2006), has been used to estimate recycled scrap streams for case studies on steel in Japan(Matsuno, Daigo et al. 2007) and the United Kingdom(Davis, Geyer et al. 2007), as well as copper(Eckelman and Daigo 2008). Most of these studies(Daigo, Matsuno et al. 2005; Yamada, Daigo et al. 2006; Matsuno, Daigo et al. 2007; Eckelman and Daigo 2008) have focused on how this methodology can overcome allocation issues when using the MFA quantities eventually for LCA analysis and therefore have not looked at how "residence time" affects recycling system behavior. The study on steel recycling in the UK(Davis, Geyer et al. 2007), however, expanded on this methodology to comment on how lifetimes and product categories can greatly influence the overall recycling rate of the system. It is assumed that the number of times the same steel can be recycled (which can be extrapolated from the calculated residence time in society) before becoming obsolete is governed by accumulation of copper and tin. But, besides the residence time of the element in question (Fe for steel and Cu), further compositional details of the scrap streams are not tracked.

Without compositional details, it is impossible to examine the effects of accumulation of tramp elements in recycled material streams over time. The research group at the University of Tokyo, however, has one of the few bodies of work that examines accumulation in recycled materials in depth, focusing mainly on steel. One such study by Kakudate *et al.*(Kakudate, Adachi et al. 2000) tracks the material flows of primary and secondary steel in Japan to estimate how accumulation of Cu will cause a growing amount of steel scrap to become obsolete. Pinch analysis, more often applied to heat transfer systems to optimize flows, was used in combination with a population balance model to project future quantities of useable scrap. A population balance model uses statistics on material flows combined with closed form numerical expressions in order to mathematically "balance" the material flows. The flow of steel was simplified to capture machinery (intended to include automotive uses) and construction products only as shown in Figure 17. In this study, it is assumed that virgin steel corresponds to convertor steel while recycled steel corresponds to electric arc furnace steel. Prompt scrap is not included in the flows although imported and exported scraps are.

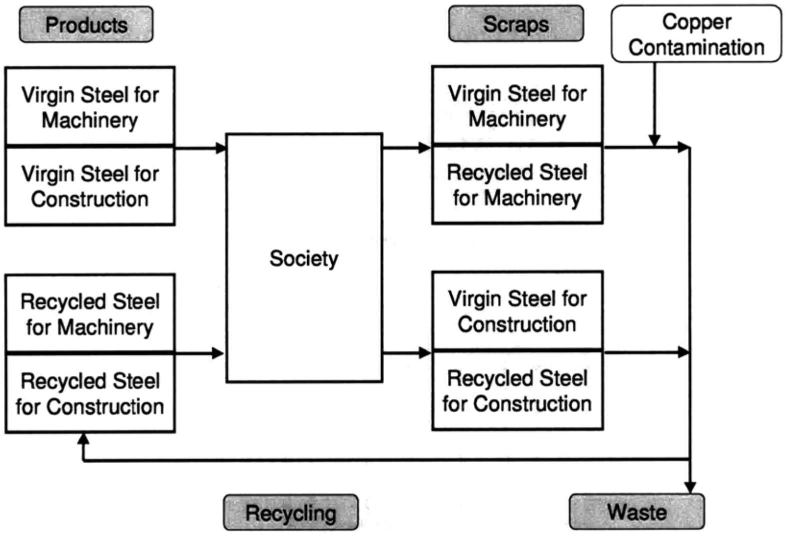


Figure 17. Schematic diagram of steel flows captured by population balance model (reproduced from (Kakudate, Adachi et al. 2000))

One assumption of particular note in this schematic is that copper only contaminates steel at end-of-life collection (i.e. neglecting alloying) and that this only occurs for machinery scrap. The authors state that copper wiring can be easily separated from steel construction scrap; however, this may not always be the case. The composition of scrap materials is inherently uncertain and therefore estimating this can be quite complex. For this study, it is assumed that the copper concentration will be 0.298 wt. % with a coefficient of variation of 25% (variance is one fourth of expected value) and will follow a normal distribution (as shown by the gray line in Figure 18). However, actual data collected for end-of-life recycled steel (also shown in Figure 18) shows a skewed distribution with a higher mean. This may indicate that the assumptions used in this model are slightly under-estimating actual copper accumulation in the recycled material.

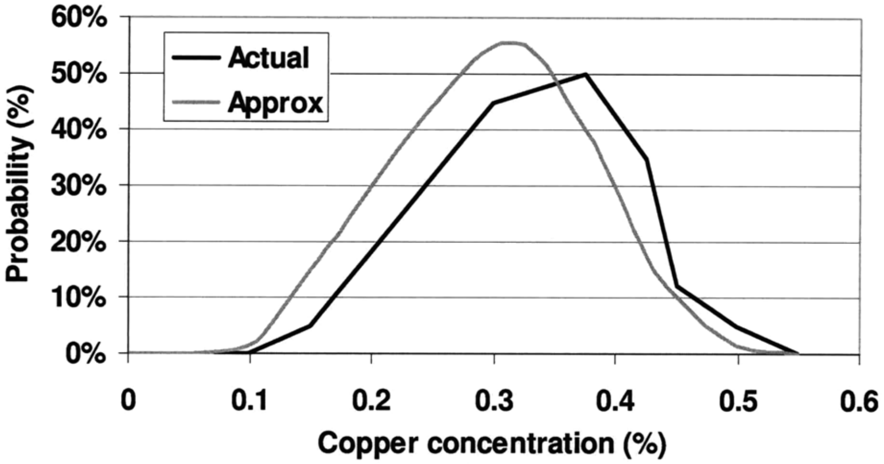


Figure 18. Assumed copper concentration distribution (approx) and actual compositional distribution of end-of-life recycled steel scrap (reproduced from (Kakudate, Adachi et al. 2000))

These assumptions together with historical data are used to forecast the production ratio of machinery to construction, domestic consumption, imports, and exports to the year 2080. Scrap availability is calculated using the population balance model and historical production data; it is a function of each product's service lifetime which was calculated to be 10 ±12.5 years for machinery and 35 ±153.5 years for construction. While this model seems to neglect dissipative uses, this may not greatly influence the results because so much scrap is being exported from Japan; this effect is investigated in more detail in a future study(Igarashi, Daigo et al. 2007). A simple decision rule is used in order to allocate the available scrap resources; it is assumed that scrap material will be used in construction until there is an oversupply. Then the remaining available scrap material will be used in machinery; the tight tolerance for copper of machinery (maximum of 0.1 wt. %) however, will eventually compositionally limit the amount of scrap that can be utilized even when diluted with primary (virgin) steel.

Figure 19 shows the projected year when the amount of available scrap of an acceptable copper composition becomes less than that which is required for machinery. The recycling ratio is the amount of scrap used in a batch plan; this quantifies the amount of dilution required to meet the machinery specifications. For example, 80(%) means that only 20% by weight of virgin steel is required in the batch. The contamination ratio is defined as the copper amount to post-consumer scrap of machinery steel, so effectively this is the weight percent copper concentration of end-of-life machinery scrap. Sensitivity analysis on these values show that decreasing the recycling ratio (increasing dilution with primary) or lowering the contamination ratio (reducing accumulation) will lead to more available compositionally favorable scrap material. Life cycle analysis (LCA) was then utilized to estimate the environmental impact of steel recycling in Japan.

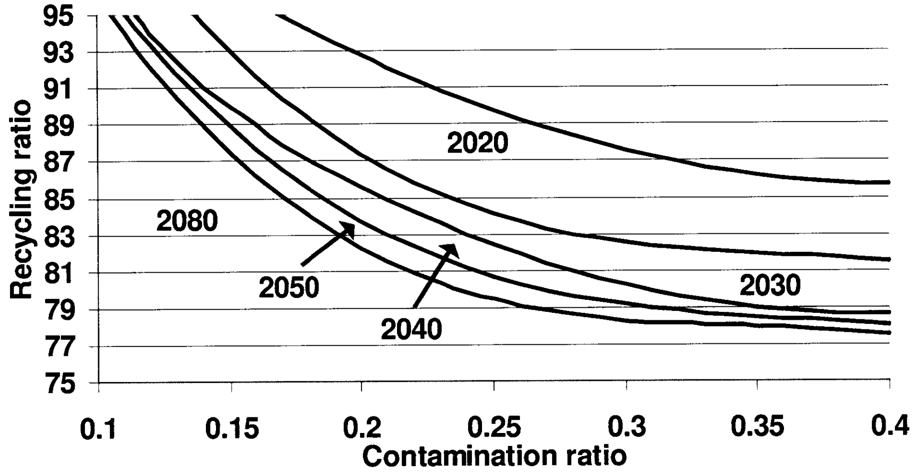


Figure 19. Year when required scrap surpasses available scrap in Japan with varying recycling ratio (amount of dilution with primary) and contamination ratio (copper concentration in end-of-life machinery scrap) (reproduced from (Kakudate, Adachi et al. 2000))

This dynamic model is used in a more recent study(Igarashi, Daigo et al. 2007) to further look at how steel scrap exports will influence tramp element accumulation in Japan's domestic scrap supply. Two cases are examined, both assuming increasing scrap exports; one assumes that the high quality (i.e. low copper content) scraps will be leaving the country while the other assumes the low quality scraps will make up the majority of exports. For the case of low quality scrap materials leaving the country, not surprisingly, accumulation of copper becomes much less of issue, specifically the amount of copper in electric arc furnace crude steel decreases over time. This may have an interesting analog for dissipative uses as well that could be investigated. For the case of high quality scrap materials being exported, the amount of copper in steel will increase until it reaches the specification limit set by the model. Increased dilution is then necessary to use these scrap steels.

The population balance model is also used to look at a larger steel case study(Daigo, Fujimaki et al. 2004), which considers more than just machinery and construction products. In this study a variety of steel products with varying lifetimes was examined, significant additions include prompt or in-house scrap, and end-of-life automotive and container scrap. In order to still solve the model numerically, however, an average copper concentration is set for all of these products except end-of-life construction scrap which is allowed to vary by time. For all three scenarios investigated (simplified these are 1) constant demand, 2) increasing exports, and 3) varying lifetimes), the amount of copper in construction fluctuates over time and eventually increases to the maximum specification for construction.

While in general this body of work from the University of Tokyo does not look at possible strategies or technologies for dealing with accumulation, one paper(Igarashi, Daigo et al. 2007) could be seen to make the case for sorting and screening technologies. In this work, the population balance model is used to examine the recycling of stainless steels in Japan. Stainless steels, which contain high amounts of chromium, can be categorized into two types: Nickel containing (austenitic) and non-Nickel containing (ferritic). The dynamic substance flow analysis provided by the population balance model and the addition of compositional details found that ferritic stainless steel scrap has extremely low collection compared to austenitic stainless steel scrap (2% vs. 95% respectively). This is mainly due to the fact that ferritic stainless steel scrap is often mixed with ordinary steel scrap because it is magnetic and this is one of the sole screening steps for the collection of stainless scraps. The authors found that if efforts are made to increase the collection of ferritic stainless scrap by only 1%, presumably by adding some form of upgrading technology, the potential CO_2 reduction could be doubled.

One article(Hatayama, Yamada et al. 2007) extends this large body of work in steel to using a population balance model to examine recycling of aluminum in Japan. In this study, eight major end uses were considered (shown with other model parameters in Table IX) and four alloying elements were tracked: Si, Fe, Cu, and Mn. These were identified as those most likely to accumulate and restrict use of recycled material. Compositional data was collected and aggregated by alloy series, assuming each alloy series composition would equal the average of the maximum specifications for selected alloys within the series[5]. These alloy series compositions were matched to end use products by rough estimation using “identifiable” and “inferable” elements. Identifiable cases would be where the alloy to end use match-up was clear, for example, 3XXX series for beverage cans and 1XXX series for foils. Inferable cases would be where the end-use products could be made of a variety of the alloy series. For these remaining cases, estimation was used in order to equate the totals of both (i.e. total of all end-use categories = total of all alloy series production).

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[5] The aluminum alloys selected for each series to create this average were not indicated.

Table IX. End use aluminum categories and assumed lifetime, yield, and collection parameters (Hatayama, Yamada et al. 2007)

End use	Distribution	Mean lifetime (yr)	Variance	Yield (%)	Collection (%)
Foil	-	-	-	10	0
Fab metal	weibull	10	3.5	10	40.3
Beverage can	-	-	-	15	-
Machinery	weibull	10	3.5	10	10
Electronics	weibull	10	3.5	10	30.1
Automotive	-	-	-	10	90
Construction	log-normal	38.7	.401	30	80
Other	weibull	10	3.5	10	30

The population balance model was used to project the availability and composition of aluminum scrap available for production out to the year 2050. It was assumed that end-of-life scrap materials would have a composition equal to the average for its end-use (i.e. no alloy separation) except for the case of automotive scrap where it was assumed engine castings would be separated from the rest of the car. For beverage cans and construction, no change in composition were observed over this time due to the assumption that only mill products would be used in their production. Compositional values that showed fluctuation are shown in Table X; the largest increases were in iron and silicon in the automotive scrap. Many large decreases were observed.

Table X. Changing compositions for several end uses and tracked elements(Hatayama, Yamada et al. 2007) Up indicates those compositions that increased and 'Down' indicates those that decreased

End use and element			2000	2010	2020	2030	2040	2050	Total
Up	Beverage can	Si	0.764	0.773	0.771	0.77	0.77	0.77	0.8%
	Automotive	Si	9.953	10.05	10.24	10.26	10.26	10.26	3.1%
	Automotive	Fe	1.117	1.183	1.194	1.195	1.195	1.195	7.0%
	Other	Mn	0.553	0.555	0.558	0.558	0.558	0.558	0.9%
Down	Machinery	Si	6.4	5.562	5.299	5.297	5.297	5.297	20.8%
	Machinery	Fe	0.856	0.778	0.755	0.754	0.754	0.754	13.5%
	Machinery	Cu	2.178	1.762	1.661	1.661	1.661	1.661	31.1%
	Machinery	Mn	0.343	0.301	0.291	0.29	0.29	0.29	18.3%
	Electrical	Si	3.264	4.046	2.649	2.646	2.646	2.646	23.4%
	Electrical	Fe	0.617	0.598	0.566	0.566	0.566	0.566	9.0%
	Electrical	Cu	1.026	0.936	0.805	0.804	0.804	0.804	27.6%
	Electrical	Mn	0.231	0.222	0.208	0.208	0.208	0.208	11.1%
	Automotive	Cu	3.705	3.695	3.676	3.674	3.674	3.674	0.8%
	Other	Si	3.106	2.776	2.313	2.312	2.312	2.312	34.3%
	Other	Fe	0.848	0.832	0.809	0.809	0.809	0.809	4.8%
	Other	Cu	1.329	1.217	1.077	1.076	1.076	1.076	23.5%

While the results for total availability of aluminum scrap for 2000 matched quite well with actual data, the authors found that their results for compositions did not match those cited in the literature from physical compositional measurements. In listing the reasons for these differences: "1) The types of products included in the scrap were different, 2) alloy composition was assumed incorrectly resulting in inaccurate estimation of scrap compositions, 3) contamination by impurities occurred in the separation and collection processes when aluminum was collected from end-of-life products, and 4) the allocation method was invalid"(Hatayama, Yamada et al. 2007), the authors capture many of the complications involved in projecting composition of recycled aluminum.

Characterizing dynamic material flows is a complex process; this complexity increases rapidly when one includes flows at end-of-life due to the many factors these flows introduce that can influence the return of recycled materials such as lifetime, collection, production, etc. However, to look at issues of compositional drift or accumulation, these additions are required. Research attempting to characterize accumulation does not necessarily have to be material flow analysis; these are works are discussed in the next section.

2.3 Other work examining accumulation

In regards to aluminum, one study by Kim *et al.*(Kim, Kim et al. 1997) examining the aging characteristics for recycled aluminum wires estimates how unwanted elements, specifically Si, Fe, Cu, Mn, Ti, and V, might increase with repeated recycling. This study simplified the accumulation of these elements to the following equation:

$$A_n = \frac{a * r * (1 - r^n)}{(1 - r)} \tag{2.2}$$

where A_n is the accumulation rate, n is the number of times recycled, a is the initial impurity concentration, and r is the mixing rate of scrap aluminum to primary aluminum. This relationship would result in accumulation trends shown in Figure 20. For mixing rates below 50%, a fairly steady state accumulation rate is observed and this study recommends recycling rates should not exceed this figure. This study does not extend the use of this equation to quantify how scrap with high accumulation will become increasingly less utilized or offer strategies to increasing the recycling rate while maintaining electrical properties.

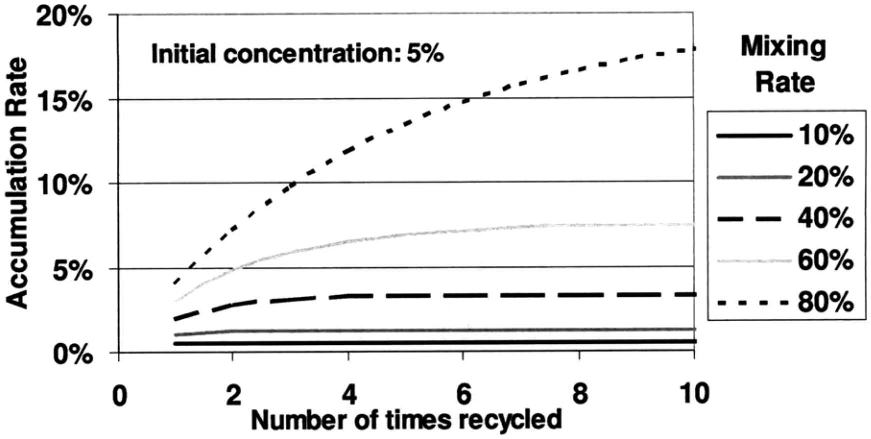

Figure 20. Trend for accumulation over multiple generations of recycling for various mixing rates and an initial impurity concentration of 5%, based on relationship suggested by (Kim, Kim et al. 1997) and shown in Equation(2.2).

One study by Viklund-White and Menad(Viklund-White and Menad 1999) is a report on impurity accumulation in copper, steel, and aluminum due to increased recycling. This report presents the negative impacts on the properties of steel (elongation, drawability, surface crack depth, etc.) and copper (resistivity, yield strength) caused by various accumulated elements. The section on steel also quantifies the improvement in these properties brought about by a few filtration technologies including magnetic, heavy media, and electrostatic separation, volatilization, melt filtration, and zone refining. However, quantification of how these improvements affect scrap utilization are not included. Menad's thesis(Menad 1999) presents environmental impacts of accumulation by using material flow analysis and LCA to track a large number of accumulated elements (Cu, Sn, Sb, As, Bi, Co, Mo, Ni, Cr, Ta, Pb, W) in steel recycling.

For the section on aluminum in (Viklund-White and Menad 1999), Fe, Mn, Mg, Cu, Si, and Sb are cited as the trace elements of most concern in secondary aluminum production. The three main upgrading methods presented for reducing these elements are separation of different alloys, dilution, and refining technologies (mainly fluxing). A quantification in regard to economic, environmental, or property improvement is not presented for aluminum, however.

Both of these studies state that repeated recycling will result in an increase of undesired impurity elements within the scrap stream. While a simplified quantification of this accumulation is useful for analysis, it very likely not capturing the complexities that are so clearly present in the material flow analysis models. The portion missing from both the MFA and these other works examining accumulation is a method to quantify the economic impact that compositional accumulation will have on secondary production. This aspect is analyzed in detail in batch planning and blending models.

2.4 Batch planning and blending

2.4.1 Linear programming for blending problems

One key portion of the recycling system missing from both general and dynamic material flow analysis is the production portfolio decisions that occur at the firm level (cf. Figure 14). Secondary producers are confronted with the wide array of scrap composition, availability, and price shown previously and must decide the mix of primary, scrap, and alloying elements to choose in order to produce their alloys to specification. Contrary to the treatment in the literature presented previously, producers do not have a static or set mix of materials based on historical statistical information but instead create dynamic batch plans daily according to changing conditions. The producer, therefore, has an important role in determining the actual composition of aluminum products.

A large variety of modeling tools are available to help support the decisions of batch planners; many producers make use of linear optimization techniques (Lund, Tchobanoglous et al. 1994). Blending problems have been addressed with linear programming models for decades(Metzger and Schwarzbek 1961). These models can improve decisions about raw materials purchasing and mixing as well as the upgrading and sorting of secondary materials (Shih and Frey 1995; Stuart and Lu 2000; Cosquer and Kirchain 2003). Producing within specification based on the initial furnace charge is a key business objective of cast-shop operators (Rong and Lahdelma 2006). Missed specifications require rework in the form of compositional additions or, even worse, dilution. Such rework is costly because it increases consumption of primary raw materials, energy, and time. To limit the incidence of rework, operators often modify mean based methods by generating batch plans based on more narrow finished goods specification targets(Bliss 1999). This narrowing of the target window creates a margin of safety around compositional specifications such that a high level of likelihood is maintained for the finished goods compositions to fall within their actual specifications. Generally, the window narrowing method is the most conservative method for a given error rate, or number of batches that fall outside of the finished goods specifications.

Work done by Debeau(Debeau 1957), in the steel industry, cautions that simply using linear programming for batch planning problems is not sufficient and suggests additional constraints to deal with variable raw materials. Often, analytical approaches may be used in conjunction with optimization to embed consideration of uncertainty in the decision-making, but generally this occurs through the use of statistical analyses that are used to forecast expected outcomes. Although this combination of statistical analysis and modeling can be powerful, it suffers from two fundamental limitations. First of all, implicit assessments based on mean expected conditions assume that deviation from that value has symmetric consequences. For many production related decisions within the cast-house, the repercussion of missing a forecast are inherently non-symmetrical. This is because dilution requires significantly more material (primary) than addition (alloying elements). Additionally, deterministic approaches generally do not provide proactive mechanisms to modify production strategies as prevailing conditions evolve. While, in the same way as window narrowing, these methods help to decrease the probability of batches being out of specification, they all share the trait of insufficient accounting for the impact on variance when combining scraps.

2.4.2 Considering uncertainty in blending plans

The wide variety of uncertainties confronting batch planners has lead to much research on the incorporation of uncertainty in linear programming models. Stochastic programming techniques encompass a large set of problems that deal with uncertainty of one form or another in the formulation. Often, this is accomplished by considering some form of probability and/or statistics within the objective function or constraints. Pioneers in the field have done work in an extremely wide range of applications including: agricultural applications such as farm management(Johnson, Tefertiller et al. 1967; Moruyama 1972) and irrigation, economics(Sengupta, Tintner et al. 1963; Tintner 1973), finance(Bradley and Crane 1972; Ziemba, Parkan et al. 1974), assignment (King 1965), facility location(Seppala 1975), inventory, water storage and reservoir management(Roseta-Palma and Xepapadeas 2004), energy, and production. Stochastic programs have been in use for solving product mix and blending problems for decades as well. Particular applications include nutrient blending for crops(Glen 1988), humans(Balintfy and Prekopa 1966), and livestock(van de Panne and Popp 1963; Rahman and Bender 1971), product mix(Hodges and Moore 1970), coal blending(Candler 1991), asphalt mixing(Martin and Lubin 1985), fertilizer mixing at a chemical plant(Ashayeri, van Eijs et al. 1994), and most prevalent, petrochemicals including gasoline(Rigby, Lasdon et al. 1995). Methods in stochastic programming are generally divided into two broad categories: single stage and multi-stage stochastic programs(Kall and Mayer 2005).

The author of this thesis has done work(Gaustad, Li et al. 2006; Gaustad, Li et al. 2006; Gaustad, Li et al. 2007; Gaustad 2009) examining the incorporation of uncertainty into blending problems and the effects this has on scrap utilization, productions costs, and product composition. This work has lead to the identification of a particularly useful technique utilizing chance constraints. Stochastic programming methods including chance-constrained variants were first formulated by Charnes and Cooper (1959; Charnes and Cooper 1963) as mechanisms to embed a more rich set of statistical information into optimization based decision models. This technique is often used when the consequences for not meeting certain constraints are unknown. Typical applications include feed mixing(van de Panne and Popp 1963; Rahman and Bender 1971), reservoir management(Azaiez, Hariga et al. 2005), nutritional planning, inventory control, metals blending(Gaustad, Li et al. 2007; Rong and Lahdelma 2008), scheduling problems(Cao, Gu et al. 2009), and water quality. Miller and Wagner (1965) were the first to apply joint probabilistic constraints, however, could only consider independent random variables on one side of the equation, not simultaneously. These mathematical techniques became more useful for real world sized problems in the 1970's, when computational power was beginning to grow rapidly. Prekopa (1972) introduced stochastic constraints as they are used currently: stochastically dependent joint probabilistic constraints. An excellent review of stochastic programming including the use of joint chance-constraints can be found in (Ruszczynski and Shapiro 2003) while a variety of recent numerical applications are available (Shih and Frey 1995; Growe 1997; Azaiez, Hariga et al. 2005).

Of the literature examining blending problems, both those that consider uncertainty and those that do not, the key missing element is the passage of time over multiple generations of batches. All of the literature presented in this section considers the blending decision at one snapshot in time and therefore cannot consider accumulation of tramp elements in the recycled material stream. Because the producer has direct influence on the resulting composition of their alloys by adjusting their batch plan, they too can influence accumulation in open and closed loop recycling. Therefore, an extension of this work to look at blending portfolios over a range of years would be necessary in order to fairly evaluate the effect of upgrading technologies.

2.5 Optimizing material flows – combining linear programming batch planning models with material flow analysis (MFA)

One body of work has looked at the useful combination of dynamic material flow analysis combined with some form of batch planning optimization. This work has been implemented to address aluminum recycling policy questions on a large scale in Europe due in part to EU directives for automotive recycling. Studies by (Schaik, Reuter et al. 2002; van Schaik, Reuter et al. 2002; van Schaik and Reuter 2004; Reuter, van Schaik et al. 2006) have used dynamic modeling and large datasets to calculate optimized recovery rates for end-of-life vehicles in order to guide operational and technological decisions by recyclers and to provide reasonable recovery expectations for recyclers, and more broadly, legislators.

The authors state that quality (meaning composition) is necessary to include in order to "determine the feasibility and limits of recycling systems, for the industry to evaluate the recyclability of (future) car designs and for the recycling industry to optimize their systems."(Reuter, van Schaik et al. 2006) Therefore, this is one of the few studies that include detailed chemical composition information for dynamic recycled material flows.

While the models used in these studies are more than likely capable; many aspects of interest to this thesis have not been examined. For example, several upgrading technologies are listed as being considered in the particle liberation model including eddy current, color sorting, magnetic, density, and air separation; however, the value of their use is neither quantified nor optimized. Proactive strategies for increasing recovery rates and recycling are not offered and little to no sensitivity analysis surrounding the many inputs and assumptions (>83,000 variables) are conducted. Sensitivity analysis of interest to this thesis would include 1) expansion to other products beyond automobiles, 2) exploration of how the linked models would differ from a time-independent analysis, 3) analysis on how the performance of the sorting methods considered impacts the results, and 4) expansion to include compositional details beyond wrought and cast fraction in order to analyze how the existence of technologies considered would effect accumulation.

In regards to accumulation, the study by Verhoef, Dijkema, and Reuter(Verhoef, Dijkema et al. 2004) utilized this dynamic mass flow model and system dynamics to evaluate the transition to a lead free solder and its impacts on the material flow and recycling of interconnected metal systems. In this work, the continued concentration of impurities in recycled material streams is given as the main reason for off-specification alloys produced. However, none of the papers from this group attempt to quantify the degree to which accumulation in recycled material streams takes place or how that impacts the optimized recycling rates and producer batch plans given.

2.6 Gap analysis summary

Table XI summarizes the gaps in the literature discussed above. The first two columns indicate the material and the region considered. For example, work pertaining to material flows may focus on a country or continent of interest; the region considered does not have as much influence in the work on blending decisions but the distinction was included anyway as it may change some of the factor inputs, such as prices. Of the work that fits under the category: end-of-life material flows, several breakdowns are listed. The first is whether or not dissipative uses are considered. This is an important aspect to consider as alloying elements present in a dissipated stream, such as steel de-oxidation will not accumulate and instead leave the recycling system entirely. The next designation is whether or not a breakdown by product is included for the end-of-life scrap flows. For these product lifetimes two things are considered, both whether or not the life is used to model the return of scrap and whether that lifetime captures some spread of uncertainty.

In terms of considering compositional details, there are varying degrees as well. "Some" indicates that there is at least a tracking by metal of composition in the end-of-life scrap stream. "Alloy series" means that composition is tracked on an aggregated AA alloy series (cf. Table I) basis, while "alloy" means specific alloy compositions are tracked. Also, designation is made whether or not some spread or uncertainty around the alloy compositions is considered as well as pick-up or outside sources of contamination.

Under the batch planning heading, the breakdown indicates which work considers portfolio selection decisions made by secondary producers. "DR" stands for decision rule and indicates that some allocation decision method is used in contrast to optimization which means that linear programming is used to find the "best" allocation decision. "UE" is the final column which indicates whether any upgrading evaluation is done. This includes both operational and technological strategies considered.

Though previous literature has used methods which individually address either environmental or technological impacts of accumulation, no study has considered the economic implications in secondary production. In order to consider important trade-offs between economic and environmental impacts, it is also necessary to consider them in combination, another aspect missing from previous work. This impact evaluation is useful to decision-makers along the production chain; in addition, analysis that can inform proactive strategies to mitigate accumulation would be a valuable contribution.

This thesis will address these gaps by combining dynamic material flows analysis comprehending end-of-life materials with optimal allocation of those materials into production portfolios using blending models. The dynamic MFA portion will allow the inclusion of compositional details for end-of-life aluminum scraps in the United States broken down by alloy. The inclusion of blending models will have the capability to examine the economic and environmental trade-offs for increased scrap utilization. Filling these gaps by developing this methodology will allow the addressing of our thesis questions:

1) How effective are operational or technological strategies at mitigating accumulation?

2) Under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams?

Table XI. Summary of previous literature gap analysis

Literature	Region	Matl.	End-of-Life Scrap Flows									Batch planning			UE[6]
			Diss[7].	By Product	Lifetime		Compositional Details					DR[8]	Opt.	Unc.	
					Consider	Unc.[9]	Some[10]	Alloy Series	Alloy	Unc.	Pick-up				
IAI study(IAI 2005)	Global	Al	X												
Boin, Bertram(Boin and Bertram 2005)	EU	Al	X	X	X										
Alcoa(Bruggink 2000; Martchek 2006)	US	Al	X	X	X										
Matsuno, et.al.(Matsuno, Daigo et al. 2007)	Japan	Steel	X	X	X	X	X								
Davis, et.al.(Davis, Geyer et al. 2007)	UK	Steel	X	X	X	X	X								
Eckelman, Daigo(Eckelman and Daigo 2008)	Global	Copper	X	X	X	X	X								
Daigo, Kakudate et al. (Kakudate, Adachi et al. 2000; Daigo, Fujimaki et al. 2004)	Japan	Steel		X	X	X	X			X		X			
Igarashi, et al(Igarashi, Daigo et al. 2007)	Japan	Steel	X	X	X	X	X			X		X			
Igarashi, et	Japan	SS[11]		X	X	X	X			X		X			X

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[6] Some upgrading technology or strategy suggestion or evaluation included

[7] Dissipative uses considered

[8] Decision rule is used to make scrap allocation – may not be optimal

[9] Uncertainty is considered

[10] Some compositional details tracked, usually at metal scale

al(Igarashi, Daigo et al. 2007)															
Hatayama, et al(Hatayama, Yamada et al. 2007)	Japan	Al		X	X	X	X	X							
Kim et al(Kim, Kim et al. 1997)	US	Al					X	X	X		X				
Menad & Viklund-White(Viklund-White and Menad 1999)	EU	Cu, Steel, Al					X				X				X
Linear blending(Debeau 1957; Metzger and Schwarzbek 1961; Lund, Tchobanoglous et al. 1994; Bliss 1999; Cosquer and Kirchain 2003)	Global	Al, Steel					X	X	X				X		
Stochastic blending(van de Panne and Popp 1963; Hodges and Moore 1970; Ashayeri, van Eijs et al. 1994; Rigby, Lasdon et al. 1995)	Global	Other, Steel					X	X	X	X			X	X	

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[11] Stainless steels

MS Thesis(Gaustad 2009)	US	Al					X	X	X	X			X	X	
Delft(van Schaik, Reuter et al. 2002; van Schaik and Reuter 2004; Reuter, van Schaik et al. 2006)	EU	Al	X	X	X	X	X						X	X	
This thesis	US	Al	X	X	X	X	X	X	X	*[12]	X	*	X	*	X

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[12] * indicates that implications for considering this will be addressed with sensitivity analysis but not focus of this work

Chapter 3. Methods

As highlighted previously, the goal of performing a dynamic, or time-dependent, valuation of upgrading technologies will require the development of a combined methodology, no single method currently encompasses both desired aspects, specifically: 1) dynamic material flows analysis comprehending end-of-life materials, and 2) optimal allocation of those materials into production portfolios using blending models. This methodology will require the combination of two specific types of models as shown schematically in Figure 21. This chapter will discuss the types of methods used to populate this model in more detail.

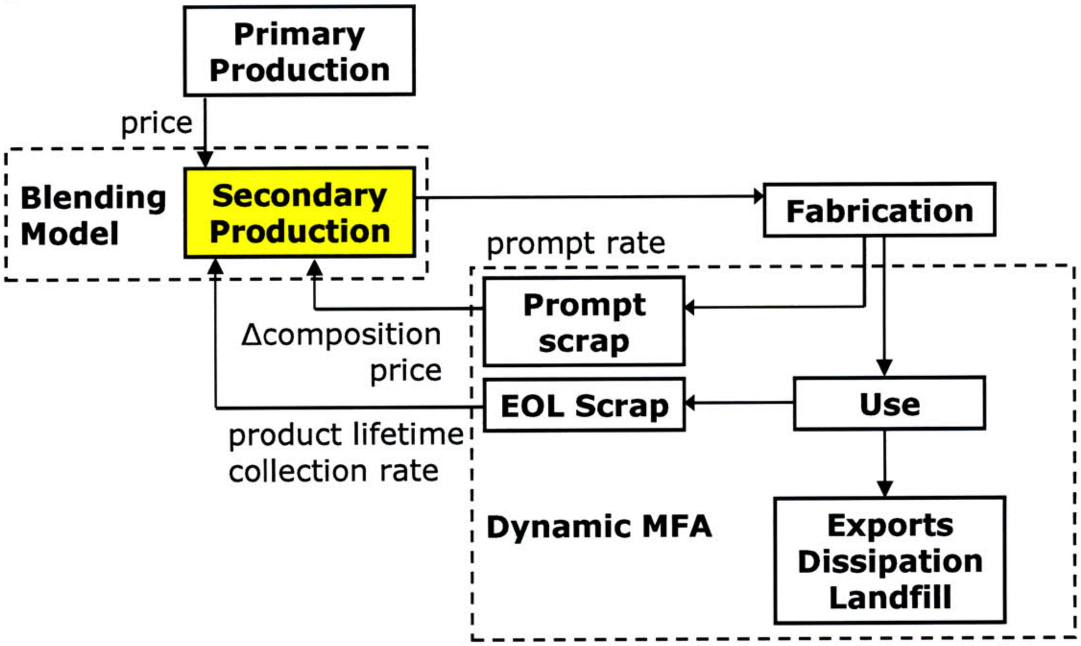

Figure 21. Schematic of aluminum material flows and models required to populate this methodology

3.1 Batch planning and blending optimization models

As discussed in the literature review section, batch planning and blending models typically use linear programming methods to identify optimal mixes of materials. Optimal can encompass a variety of goals: highest profits, lowest production costs, or highest use of recycled materials for example. The constraints on this goal can be very different for different producers as well. This section will give the mathematical details on the types of blending models used through-out this thesis analysis. A trade-off exists between the addition of information to the linear programming method and the computational complexity of the models which will be discussed more quantitatively in section 3.4.

3.1.1 Linear optimization

A linear optimization model, i.e. a mathematical program with no non-linearities, is the simplest blending model in terms of computational complexity. This batch planning problem can be formulated as follows in Equations (3.1) through (3.5). The goal of this model is to identify the production plan, referred to subsequently as a batch plan, that will minimize the overall expected production costs (*C(x)*) of meeting finished good compositional specifications through optimal and efficient use of primary and secondary raw materials (Eq.(3.1)). It should be noted that for this particular objective, although the cost will be referred to as the production cost, it is actually the cost of materials only. This does not include other processing costs such as energy, labor, tooling, equipment, etc. To more accurately capture the behavior of a recycling operation, this simple objective is subject to a number of specific constraints. Firstly, raw materials cannot be prescribed in the batch plan in excess of the quantity available (Eq.(3.2)). Secondly, the batch plan must lead to production quantities that meet or exceed the established target for each alloy (Eq.(3.3)). Finally, the composition of the batch plan must fall within the finished alloys specifications required (Eqs. (3.4) & (3.5)).

Min:
$$\sum_i C_i X_i \tag{3.1}$$

Subject to:
$$\forall_i \quad \sum_j x_{ij} = X_i \le A_i \tag{3.2}$$

$$\forall_j \quad \sum_i x_{ij} = B_j \ge M_j \tag{3.3}$$

$$\forall_{j,k} \quad \sum_i x_{ij}\bar{\varepsilon}_{ik} \le B_j \varepsilon_{jk}^{\max} \tag{3.4}$$

$$\forall_{j,k} \quad \sum_i x_{ij}\bar{\varepsilon}_{ik} \ge B_j \varepsilon_{jk}^{\min} \tag{3.5}$$

All other variables are defined below:
C_i = unit cost ($/T) of raw material *i*
x_{ij} = mass of raw material *i* used in making finished good *j*
X_i = mass (kt) purchased raw material *i (both primary and scrap)*
A_i = mass of raw material *i* available for purchasing
$\bar{\varepsilon}_{ik}$ = average mass element *k* in raw material *i*
B_j = mass of finished good *j* produced
M_j = mass of finished good *j* demanded
$\varepsilon^{max}{}_{jk}$ = maximum mass element *k* in finished good *j*
$\varepsilon^{min}{}_{jk}$ = minimum mass element *k* in finished good *j*

3.1.2 Chance constrained stochastic programming

In the context of cast-shop batch planning, the chance-constrained method allows the compositional constraints to be modified such that 1) the model embeds knowledge of both the mean and variance of available raw materials and 2) the user can query the model for optimal solutions which provide a specified level of confidence for meeting the compositional specifications. This method relates the desired level of confidence to the underlying standard deviations observed in the sampled raw materials. With the understanding that the compositional constraints will not always be satisfied due to inherent uncertainty, they can be rewritten as probabilistic expressions and transformed into their deterministic equivalents. For the batch mixing problem at hand, the constraints expressed in Equations (3.4) and (3.5) are transformed into Equations (3.6) and (3.7):

$$\begin{aligned}&\Pr\left\{\sum_{i} x_{ij}\bar{\varepsilon}_{ik} \le B_j \varepsilon_{jk}^{\max}\right\} \ge \alpha \\ &\rightarrow \forall_{j,k} \ \sum_{i} x_{ij}\bar{\varepsilon}_{ik} + X(\alpha)\Big(\sum_{i}\sum_{l} \rho_{(\varepsilon)ilk}\sigma_{(\varepsilon)ik}\sigma_{(\varepsilon)lk}x_{ijk}x_{ljk}\Big)^{1/2} \le B_j \varepsilon_{jk}^{\max}\end{aligned} \tag{3.6}$$

$$\begin{aligned}&\Pr\left\{\sum_{i} x_{ij}\bar{\varepsilon}_{ik} \ge B_j \varepsilon_{jk}^{\min}\right\} \ge \beta \\ &\rightarrow \forall_{j,k} \ \sum_{i} x_{ij}\bar{\varepsilon}_{ik} + X(1-\beta)\Big(\sum_{i}\sum_{l} \rho_{(\varepsilon)ilk}\sigma_{(\varepsilon)ik}\sigma_{(\varepsilon)lk}x_{ijk}x_{ljk}\Big)^{1/2} \ge B_j \varepsilon_{jk}^{\min}\end{aligned} \tag{3.7}$$

Where the additional variables are defined as:

$\sigma_{(\varepsilon)ik}$ = standard deviation of the composition (ε) of element k in raw material i

$\rho_{(\varepsilon)ilk}$ = correlation coefficient between composition (ε) of element k in raw materials i and l (ρ_{il} = 1 when $i=l$)

$X(\_)$ = inverse of a normalized cumulative Gaussian distribution function

α = likelihood that the actual composition will fall below the upper limit of final alloy composition

β = likelihood that the actual composition will fall above the lower limit of final alloy composition

Of these, the ones that may require further clarification are α, β, and $X()$. The statements Pr(.) state that those constraints which were originally required to be strictly satisfied are now only satisfied α and β percent of the time. Thus α and β are desired levels of confidence factors which the operator can use to adjust his or her sense of importance for that particular elemental composition to be within specifications. Specifically, α and β represent the likelihood that the batch plan identified by the model will result in a composition that is lower than the upper compositional limit and greater than the lower compositional limit, respectively. The function $X(.)$ is the inverse of a normalized cumulative Gaussian distribution function[13] which characterizes the relative distance from the mean that corresponds to the designated level of likelihood. This relates the underlying raw material composition standard deviations to the desired level of confidence. The symbol ρ_{ij} represents the correlation between the fluctuations in composition of raw material i and j. By definition $\rho_{ij} = 1$ when $i = j$.

The addition of uncertainty to the batch planning models not only allows for batch plans that have a confidence interval for being within specification but also allows for sensitivity analysis around composition. This is a significant addition as these compositions are difficult to characterize and will inherently be uncertain as outlined in Chapters 1 and 2.

3.1.3 Multi-generation optimization programming

A time-dependent analysis of upgrading will require a blending model that comprehends more than one generation of scrap materials. Specifically, the composition of the available scrap materials will be a function of the composition of the finished alloys from the time period before. Mathematically, this formulation would be as follows:

Min:

$$\sum_{z}\sum_{i} C_i X_{iz} \tag{3.8}$$

Subject to:

$$\forall_{i,z} \quad \sum_{j} x_{ijz} = X_{iz} \le A_{iz} \tag{3.9}$$

$$\forall_{j,z} \quad \sum_{i} x_{ijz} = B_j \ge M_j \tag{3.10}$$

$$\forall_{j,k,z} \quad \sum_{i} x_{ijz}\bar{\varepsilon}_{ikz} \le B_j \varepsilon_{jk}^{\max} \tag{3.11}$$

$$\forall_{j,k,z} \quad \sum_{i} x_{ijz}\bar{\varepsilon}_{ikz} \ge B_j \varepsilon_{jk}^{\min} \tag{3.12}$$

$$\forall_{j,k,z} \quad \frac{\sum_{i} x_{ijz}\bar{\varepsilon}_{ikz}}{\sum_{i} x_{ijz}} + \left(a_k * \frac{\sum_{i} x_{ijz}\bar{\varepsilon}_{ikz}}{\sum_{i} x_{ijz}} \right) = \bar{\varepsilon}_{ik(z+1)} \tag{3.13}$$

$$\forall_{j,z} \quad \sum_{i} x_{ijz} = X_{jz} * P_j = A_{i(z+1)} \tag{3.14}$$

Additional variables are defined below:

z = generation

a_k = accumulation rate of element k

P_j = prompt scrap rate of finished good j

Because the scrap composition is a function of the previous period's product composition, the non-linearities will increase exponentially with the number of generations considered. This will cause the problem to grow in computational

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[13] Other statistical distributions can also be assumed.

complexity quite rapidly. Having an overall optimum also raises several stakeholder issues as well, in reality, most producers make blending decisions based solely on the currently available scrap and subsequent time period's demand. These stakeholder issues, combined with the computational complexity problem, make it necessary to implement the blending model independently each year using data that is supplied by the dynamic material flow analysis. The interaction of these models will be described in section 3.5.

3.2 Monte Carlo simulations

To test the optimal batch solutions given by the blending methods described previously, Monte Carlo simulations were run to evaluate the robustness of batch plans to variation in the composition of incoming scrap materials. The Monte Carlo method uses pseudo-random numbers (i.e. not truly random in the sense that they are generated by numerical algorithms) to statistically simulate random variables, in this case, scrap composition. Unless otherwise noted, 10,000 simulations were run for each compositional element tracked and the total number of times a batch resulted in being out of specification were recorded as the error rate for a particular batch plan.

3.3 Dynamic material flow analysis

A typical material flow analysis is a snapshot of all of the flows of a certain material in a specific region for a set time period, typically one year. For example, an aluminum material flow analysis would quantify in the magnitude of the flows of the following areas: primary production, secondary production, new and old scrap recycled, and products entering stocks in use as shown schematically in Figure 22. A dynamic material flow analysis captures the magnitude of these flows over multiple years as well as projects what the magnitude of these flows may be in the future. To project the magnitude of finished products in the future, the historical demand and consumption is explored statistically using regression analysis. The resulting regressed trends are used for projections. To project the flow of future returning scraps, historical demand is used, along with the lifetime and collection rates for the product categories that are captured in total stocks-in-use.

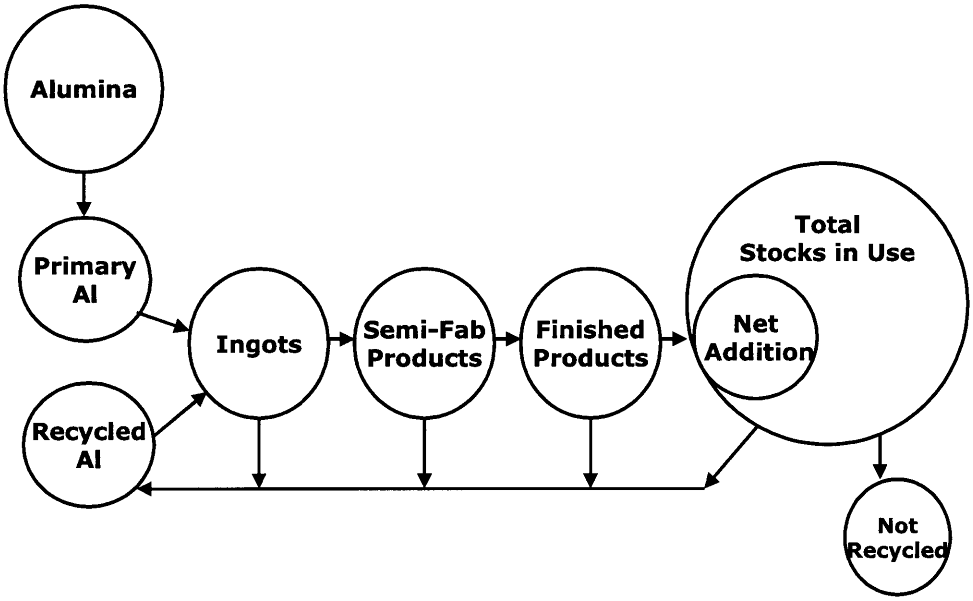


Figure 22. Schematic of flows captured by typical MFA analysis, reproduced roughly from (Boin and Bertram 2005; IAI 2005; Graedel, Harper et al. 2006)

For a specific example of how end-of-life scrap material availability would be projected, consider the automobile. The historical demand of cars in the United States would be collected and the trend would be regressed to project future demand for cars. The average lifetime for a car is approximately 15 years so this would be the average amount of time between when a car is produced and when it reaches end-of-life. It is assumed that this lifetime will follow a normal distribution and therefore cars produced in a specific year would be returned in years surrounding year 15 according to the magnitude of standard deviation assumed for the lifetime. Some percentage of these cars reaching end-of-life will then be collected for recycling. This combination of historical production, average lifetime, and rate of collection thus determines the dynamic availability of automotive scrap over time.

3.4 Considering uncertainty over multiple generations – a note on computational complexity

The three main inputs that scale the size of the batch mixing problem are the number of finished alloys j, number of raw materials i (this includes scrap, primary aluminum, and alloying elements), and the number of compositions k being tracked (elements such as Si, Mg, etc.). For the linear, deterministic method the total number of decision variables will be i x j ($O(mn)$) and the total number of constraints will be i (availability of raw materials) + j (batch size constraints) + 2 x j x k (compositional constraints); this will be dominated by the compositional terms and therefore will be $O(2mn)$. For the chance constrained method, the number of decision variables will remain unchanged but the number of compositional constraints will now double due to the addition of the variance parameters described in section 3.1.2 and will therefore be $O(mn^2)$. More significant to the scaling, however, is that the chance constrained method includes the introduction of both non-linear decision variables and constraints which will greatly affect the computational intensity.

Table XII. Projected scaling results for three blending models (Det-deterministic linear program, CC-chance constrained, Multi- multiple period) small scale case and typical production size case

	Small scale case			Production size case		
	Det	CC	Multi	Det	CC	Multi
Products *j*	2	2	2	15	15	15
Raw Materials *i*	2	2	2	25	25	25
Compositions *k*	2	2	2	15	15	15
Periods *z*	NA	NA	2	NA	NA	6
Decision Variables	4	4	1500	375	375	4500
Availability	2	2	25	25	25	25
Batch Sizes	2	2	15	15	15	15
Composition	8	16	16	450	900	2700
Total Constraints	12	20	56	490	940	2740

Actual scaling of these models may differ significantly from the projected scaling due to the specific formulation as well as the algorithms used for solving which may vary with different optimization software packages. To test these formulations, Lingo by Lindo Systems was used. Two key metrics used to indicate computational complexity are storage and iterations-to-convergence. Storage, or the amount of memory that is allotted to generating the matrices needed to solve the problem can be an indication of poor performance of some methods due to the number of cache misses caused by moving parts of the problem into smaller computer storage sections. Iterations-to-convergence is the best indication of time to solve; time is not used as some machines can perform iterations much faster than others. Day-to-day operational decision-making requires these methods to not be prohibitively computationally expensive in terms of time.

As shown in the projected scaling, the number of products, raw materials, and compositions tracked will determine the computational complexity. Figure 23 shows how memory increases with increasing number of products considered for the deterministic, chance-constrained stochastic optimization, and the multi-generation optimization methods. One can see that optimizing over all the generations considered requires substantially more memory than the stochastic and deterministic single generation models. However, while the chance-constrained method doesn't appear to require much more than the deterministic method compared to the multi-generation, this difference (approximately 2X at 30 products) is still significant.

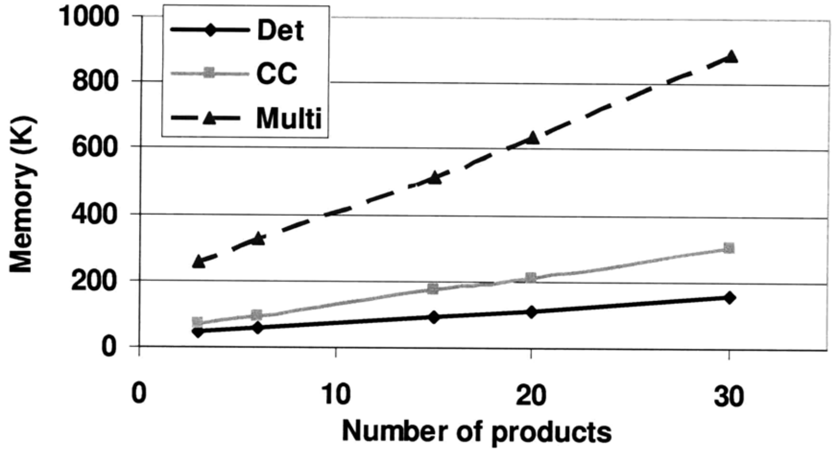


Figure 23. Comparison of memory (storage) required for the three different types of blending models with increasing numbers of products

More telling in terms of computational complexity analysis is the number of iterations to convergence. Figure 24 shows how this varies for the three methods with increasing number of compositions; the deterministic method is shown in gray on the secondary axis. Note that the chance-constrained and the multi-generation methods are shown on a log scale; both of their computational complexity is significantly higher than a linear programming blending model with no non-linearities. This is the case for increasing number of raw materials as well, where raw materials include the number of scraps, primary aluminum, and alloying elements. Figure 25, also on a log scale, shows that the chance-constrained method is significantly more computational complex compared to the linear, deterministic model.

This computational complexity analysis would motivate the usage of a deterministic blending model when considering multiple generations. However, for a time-independent analysis, because multiple generations are not an issue, the chance constrained method affords a means to examine sensitivity analysis surrounding resulting variance in the composition.

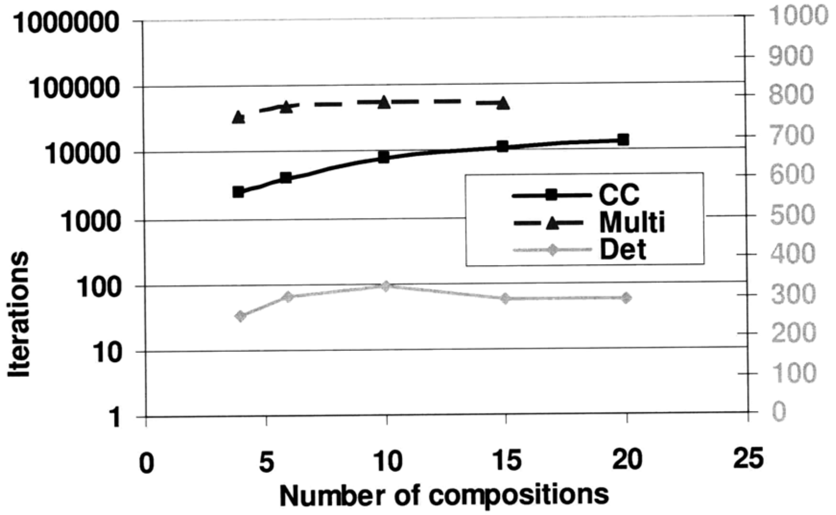


Figure 24. Comparison of number of iterations to convergence required for the three different types of blending models with increasing number of compositions tracked

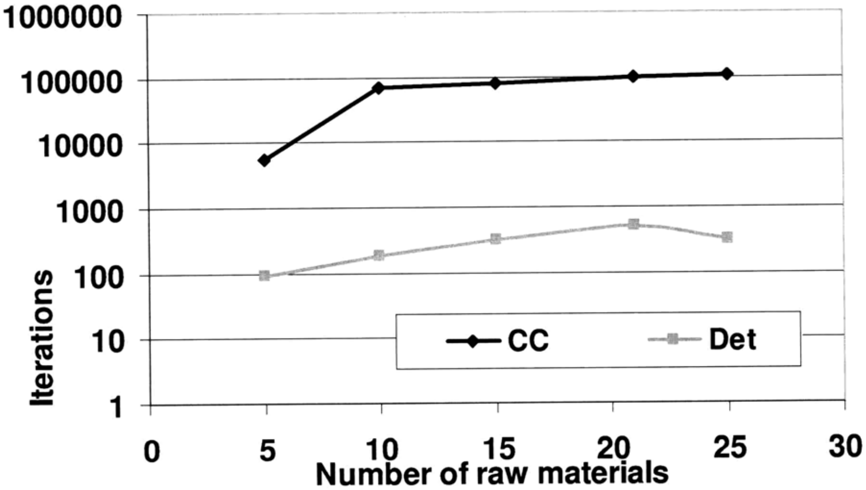


Figure 25. Number of iterations to convergence comparison of chance constrained and deterministic batch planning models with varying number of raw materials (includes scraps, primary aluminum, and alloying elements)

3.5 Model combination

The combination of dynamic material flow analysis and blending models is a unique methodology. These two models work in tandem according to the Figure 26 schematic. In a given year, the dynamic material flow analysis will provide the magnitude of specific scraps available and their composition. The blending model can then select from these available scraps as well as primary aluminum and alloying elements. The production portfolio will be the demand for alloys in the following year which is determined from the regression of historical demand data for each alloy being produced. The deterministic, linear optimization blending model is then run using this information and will result in the optimal allocation of these raw materials for each alloy produced. The Monte Carlo simulations can be used at this stage to test the optimal batch plan under conditions of uncertain recycled material composition to ensure that the resulting batch plan will produce all alloys to within specification. The resulting production amount as well as composition of these alloys according to the results from the optimal allocation are then fed back into the dynamic material flow analysis. These products will become scrap material in subsequent years according to the lifetime of the product in which the alloy is placed. The application of this dynamic material flow analysis methodology to the aluminum recycling system will be detailed in chapter 6.

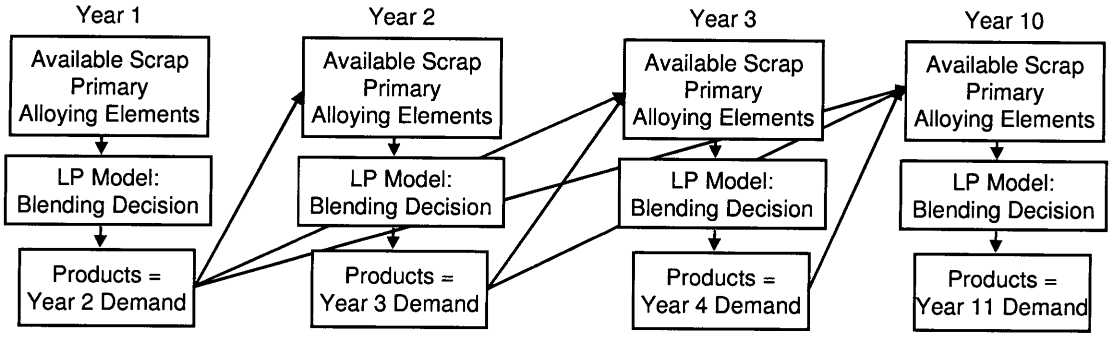


Figure 26. Schematic of model combination, steps in the methodology

Accurately valuing upgrading technologies and their ability to mitigate accumulation over time requires the combination of several methods; these methods were detailed above. The resulting combined methodology was applied to two specific upgrading technology cases to compare their values using both a time-independent and dependent analysis. These specific cases were selected from the wide array of upgrading technologies available. The next chapter will first detail the types and capabilities of upgrading technologies available both in industry and in the research and development phase. Subsequent chapters will then apply the methods described in this chapter to the specific upgrading cases.

Chapter 4. Upgrading technologies for aluminum scrap

Accumulation of undesired impurities in recycled scrap streams is widespread and problematic as outlined in Chapter 1 and 2. An introduction to the operational and technological strategies that exist for dealing with this negative impact on recycling due to accumulation has been discussed. The addition of batch planning models to the dynamic material flow methodology ensures that operational strategies are not ignored. Such operational strategies include two prevalent current solutions: dilution and down-cycling. Dilution with primary aluminum is the most common; this has a negative impact on recycling as the required dilution results in a compositionally determined cap to recycling rates. "Down-cycling", where materials are recycled into lower value products, is another common method of addressing highly contaminated secondary materials; this may enable higher usage of recycled materials but could negatively effects recycling economics. A specific example of down-cycling is when wrought scrap is used in cast products due to their ability to accommodate higher silicon contamination.

More importantly, the inclusion of batch planning captures another operational solution: optimal allocation of recycled scrap materials. As important as these operational strategies are to mitigating the negative effects of accumulation, there are far more technological strategies available to the producer when these operational strategies become ineffective. These upgrading technologies will be categorized by the main mechanism in which they remove unwanted elements either by 1) physically separating solid scrap streams to prevent co-mingling of metals and elements or, 2) refining technologies that attempt to chemically or kinetically move unwanted particles and elements in the melt.

4.1 Pre-melt technologies: physical separation

While physical separation technologies can be applied to a wide range of scrap streams, they are typically used for scrap that has been shredded(Wilson, Veasy et al. 1994). The majority of automotive scrap, for example, goes through some sort of shredding process before being sold to secondary re-melters. These automotive hulks will be a focus of much of the upgrading technologies as they make up a large portion of end-of-life recycled scraps(Kelly and Matos 2006). There are approximately 200 shredders operating in North America; most use large hammer mills to smash scraps such as end-of-life automotive hulks into pieces typically smaller than four inches(Rousseau and Melin 1989). Before using some of the more advanced physical separation technologies described below, general separation by particle size is often applied using various screening methods. De-lacquering processes are also quite common in which the scrap is heated to remove paints, paper and plastic labels, and other coatings.

4.1.1 Magnetic

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

4.1.2 Air separation

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

4.1.3 Eddy current separation

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

$$i=\frac{(K*\nu*B)*\sigma*A}{L} \tag{4.1}$$

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

Table XIII. Electrical conductivity of several metals

Electrical Conductivity $*10^6$ $(\Omega\text{cm})^{-1}$		Electrical Conductivity $*10^6$ $(\Omega\text{cm})^{-1}$	
Mn	0.006	Fe	0.093
Sb	0.028	Ni	0.143
Pb	0.048	Zn	0.166
Al	0.067	Mg	0.226
Cr	0.077	Cu	0.596
Sn	0.091	Ag	0.630

4.1.4 Sink-float/heavy media separation

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

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

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

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

4.1.5 Color sorting – by hand and spectrographic technologies

Color sorting takes advantage of the color difference between scraps to separate zinc, copper, brass, and stainless steel from aluminum in a non-ferrous scrap streams. The most basic application of color sorting is when metals are sorted by hand, a prevalent practice in countries with low labor costs. United States exports of scrap to these countries have been growing substantially in recent years (Figure 27); the value of scrap exported to Taiwan, Korea, Hong Kong, and China has grown five fold in five years. Empirical evidence of the capabilities of hand sorting beyond observation have not been reported, however, it is estimated that workers in China can achieve accuracies up to 99% when sorting non-ferrous automotive shred(Minter 2006). Because of distinctive surface characteristics that differ between them, it has also been cited that hand sorting is capable of sorting wrought and cast aluminum fractions(Rao 2006).

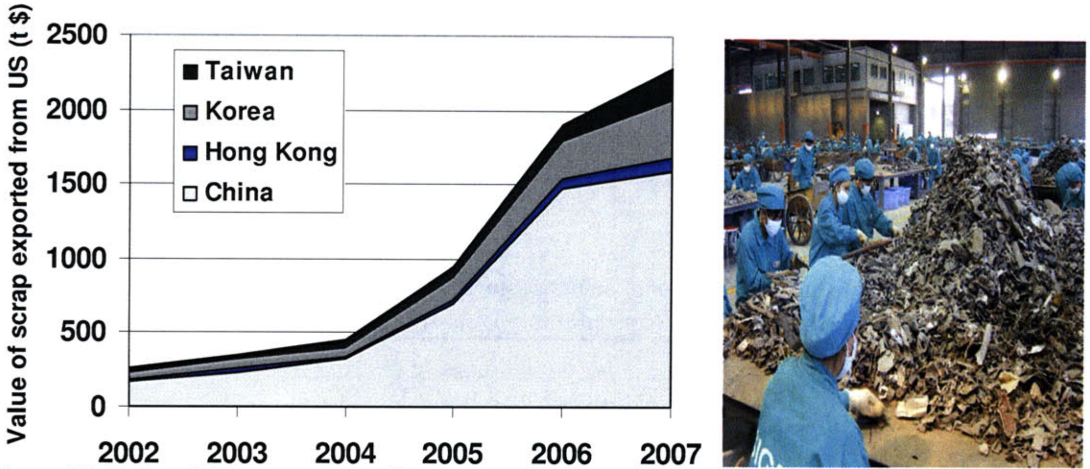


Figure 27. Value of US scrap exports by country (Plunkert 2005); photo of scrap sorting facility in Shanghai

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

4.1.6 Other spectrographic techniques

Spectroscopy has become more widely used for identification and sorting of aluminum and magnesium alloys in recent years. In this technology, various scrap pieces pass by an array of sensors which trigger one of three main activation methods: 1) x-rays, 2) neutron flux, and 3) pulse laser. The relevant source hits the metal which produces an emission: x-ray fluorescence by the x-rays, gamma ray fluorescence by the neutron flux, and an optical emission for the pulse laser. These spectra are read by varying types of detectors and a computer then sends a signal which sends the piece of scrap to the appropriate bin.

Hand-held x-ray fluorescence (XRF) units are currently in use but, their high cost prevents pervasive use in scrap processing yards. For XRF, the spectral ratios of scrap materials are determined according to their major alloying element because aluminum has a very low characteristic radiation which cannot be read unless under vacuum. Studies on the commercial applicability of XRF in sorting have shown it to be capable of separating into major alloy family but cannot determine specific alloys(Krotkov, Satayev et al. 1993). Neutron activation requires long exposure times to the neutron flux due to its limited intensity and therefore has not been commercialized. One technology in particular, laser induced breakdown spectroscopy (LIBS) which utilizes a pulse laser and optical emission spectroscopy, has shown great promise for sorting of wrought and cast aluminum(Gesing, AuBuchon et al. 2003). This technology will be discussed later in this chapter with a case study examining the value of using laser sorting for separation of co-mingled, shredded aerospace scraps.

4.1.7 Hot crush

The hot crush process is a thermal-mechanical separation method that is currently one of the few ways to successfully separate wrought and cast aluminum alloys in industry. This process takes advantage of the low eutectic temperature of casting alloys which are high in silicon (Figure 28). Because the cast alloys have a lower melting temperature than the wrought alloys, holding or "soaking" the mixed scrap at a temperature below the eutectic (~550°C) will result in a weakening of the castings along their grain boundaries. A subsequent mechanical crushing or grinding then causes those alloys to break and they can be separated from the wrought with various particle size screening processes. A positive side effect of the heating phase is that painted scrap also experiences some delacquering. Studies have shown the technology to be 96% effective in separating a mixed wrought-cast stream(DeGaspari 1999). However, successful segregation requires that the initial scraps be fairly large in size as the screening portion relies on the wrought aluminum remaining that way. Therefore, separation of shredded scrap streams or smaller products is not possible.

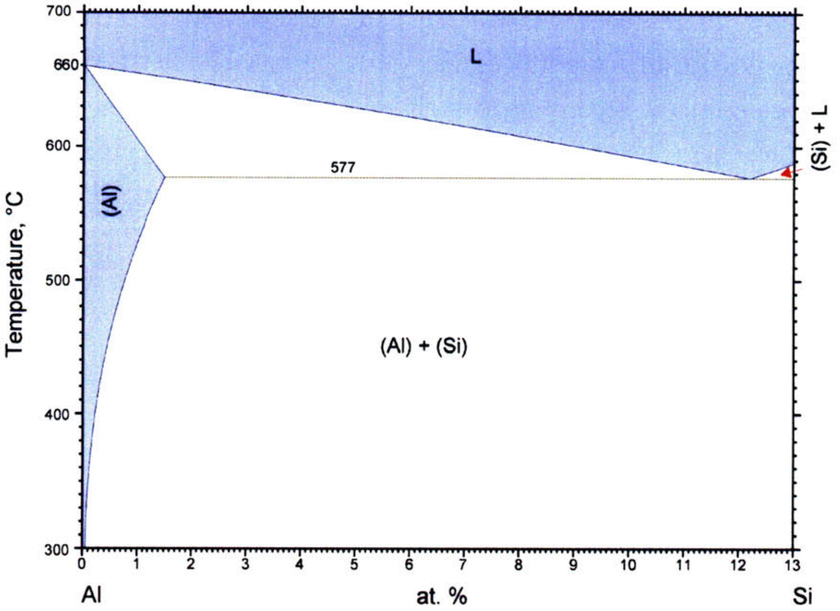


Figure 28. Binary phase diagram for aluminum-silicon system 13 at. % Si = 13.5 wt. % Si (© ASM International 2006. Diagram No. 979856)

4.1.8 Summary of physical separation technologies

Often, particularly in the case of shredded automotive hulks, co-mingled scrap will be subjected to a variety of these physical separation technologies to achieve a relatively pure aluminum scrap stream for melting. The technologies used and their use sequence varies between different secondary producers and scrap processors. A typical physical separation sequence is shown in Figure 29. Optimal ordering of these technologies has not been investigated in current literature and will be discussed as a possible extension to evaluating upgrading technologies in the future work section.

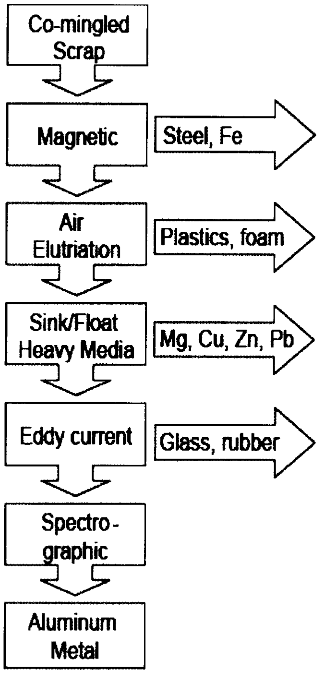


Figure 29. Diagram of possible physical separation sequence for co-mingled scrap, particularly automotive

4.2 Melt technologies: refining

Once scrap material enters the furnace, physical separation technologies can no longer be applied. Technologies aimed at removing impurities from the melt are quite prevalent. Melting is a metallurgical process and is therefore governed by the laws of thermodynamics. The removal of unwanted elements in the scrap stream is dictated by the energy considerations of the melt process. In the case of aluminum, the thermodynamic barrier to the removal of most elements is quite large. Figure 30 shows an Ellingham diagram for alumina reduction illustrating the Gibbs free energy change as a function of temperature for various oxidation reactions. The main reaction of note, reduction of alumina to aluminum metal as expressed in Eq. (4.2) is the thick black line in the middle of Figure 30. One can see that the majority of equilibrium lines are at a higher free energy than aluminum, indicating that no partial pressure of oxygen would allow them to be oxidized into the slag. Of the elements shown here, only magnesium and calcium can be effectively removed from the melt by simple oxidation. In the case of iron and by extension, steel as shown in Figure 30, only copper and nickel have a higher free energy than iron oxide reduction and therefore all other elements listed can be efficiently removed from the melt.

$$\frac{4}{3}\mathrm{Al} + \mathrm{O}_2 \rightleftarrows \frac{2}{3}\mathrm{Al}_2\mathrm{O}_3 \qquad (4.2)$$

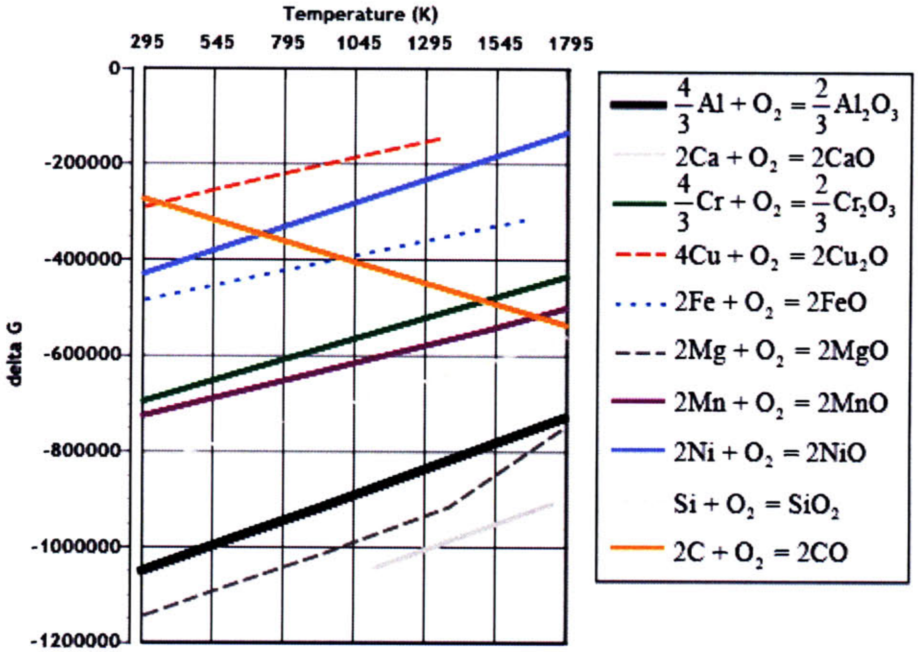


Figure 30. Ellingham diagram for various reactions(Kubaschewski, Evans et al. 1979; Ragone 1995)

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

Table XV. Melting temperature of several metals

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

4.2.1 Fluxing

The most common technology aimed at removing impurities from the melt is simple fluxing. Fluxing is when various compounds (usually inorganic salts), chemicals, and gases are added to: 1) reduce oxidation, 2) encourage certain elements to migrate into the dross, or top layer of the melt, 3) increase the fluidity or wettability of the melt which facilitates the separation of inclusions, 4) remove hydrogen and nitrogen gas, and 5) remove Ca, Sr, Na, Mg, and Li(Utigard, Friesen et al. 1998). Fluxes are useful in removing calcium, magnesium, sodium, etc. from aluminum by serving as catalysts for their equilibrium oxidation reactions (cf. Figure 30). They will form more stable chlorides and fluorides than aluminum which can then be removed from the melt through sedimentation or dross formation depending on their resulting density. For example, addition of $AlCl_3$ will cause the following reaction: $Mg + Cl_2 \rightarrow MgCl_2$. $MgCl_2$ has a lower density than liquid aluminum and will migrate to the dross. The most common solid fluxes in use include KCl, NaCl, NaF, AlF_3, and $MgCl_3$ and common fluoride salt additions such as Na_3AlF_6 (cryolite), CaF_2, and Na_2SiF_6(Utigard, Friesen et al. 1998) Many of the fluoride fluxes are capable of slightly dissolving thin oxide films and therefore expose aluminum metal improving the metallic yield. While the use of fluxes is prevalent in secondary aluminum processing, there are still several drawbacks. One limitation is that a large amount of flux may be required to achieve efficient reactions. For example, studies estimate that for a 100% efficient reaction, 2.95 kg of chlorine would be required to remove 1.0 kg of magnesium. Therefore, for a typical wrought 5XXX or 6XXX series scrap melt, it would require up to 120 kg of chlorine gas to remove the magnesium from one metric ton of aluminum(Utigard, Friesen et al. 1998). Also, chlorides and fluorides produce toxic and dangerous gases which must then be filtered from emissions.

4.2.2 Hoopes process

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

4.2.3 Low temperature electrolysis

Low temperature (~100°C) electro-refining methods have been shown to produce aluminum of 99.89% purity(Kamavaram, Mantha et al. 2003). The lower temperature electrolysis can provide significant energy savings over the Hoopes process. For this, anhydrous aluminum chlorides are used to form an ionic liquid; the aluminum that needs to be refined is placed in this solution and becomes the anode. The purified aluminum is electrodeposited on a pure aluminum or copper cathode according to the following electro-chemical reactions: 1) Al alloy (anode) + $7AlCl_4^-$ → $4Al_2Cl_7^-$ + 3 e^- and 2) $4Al_2Cl_7^-$ + 3 e^-→ pure Al (cathode) + $7AlCl_4^-$. This electrolysis is capable of removing Mn, Fe, Si, Cu, Zn, Ni, and Pb(Kamavaram, Mantha et al. 2003). Because the ionic liquids are stable at the lower operating temperature, they can be reused thus making the process more environmentally friendly.

4.2.4 Segregation

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

4.2.5 Distillation technologies

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

Table XVI. Boiling point of several metals

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

Zinc distillation is used to upgrade zinc containing metallic scrap streams in the zinc secondary processing industry. However, its extension to removing zinc from aluminum melts is still in the research and development stage. One study showed that a continuous agitation zinc distillation process was capable of reducing an aluminum melt with >3 wt.% zinc to less than 0.1 wt.%(Ohtaki, Arakawa et al. 2000). The mass transfer coefficient, K, effectively the zinc removal rate, was calculated as:

$$K = \ln\left(\frac{C}{C_o}\right)\frac{V}{At} \tag{4.3}$$

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

4.3 Inclusion and hydrogen removal

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

4.3.1 Sedimentation

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

$$V_s = \frac{2(\rho_{particle} - \rho_{fluid})}{9\mu} g r^2 \tag{4.4}$$

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

4.3.2 Flotation

Also referred to as degassing, flotation is used to remove entrapped hydrogen from aluminum casting melts. Hydrogen is the only gas that has solubility in aluminum; this increases with melt temperature. It is the main cause of porosity in solidified castings and ingots(Lin and Hoch 1989). For the flotation process, a chlorine and argon gas mixture is injected in the bottom of the melt, as the bubbles rise, the hydrogen atoms diffuse to the bubble surface and produce hydrogen gas within thus expanding the bubbles. When the bubble reaches the melt surface, the hydrogen gas is released. The bubbles also help to encourage other low density inclusions to migrate to the dross layer at the surface of the melt. The small percentage of chlorine in the gas will also help to remove alkali impurities as outlined in the fluxing section (3.2.1). The injection of fluxing agents combined with degassing or flotation technologies is the subject of a large body of research(Veasey, Wilson et al. 1993).

4.3.3 Filtration

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

4.4 Summary of available upgrading technologies

Table XVII summarizes the technologies covered, their capabilities, industry penetration, target scrap stream, and whether it is targeted at the melt (liquid) or solid scrap form. It should be noted that many more technologies not covered here are in the research and development phase. The uncertainty surrounding scaling up these technologies combined with the wide range in technologies already available highlights the fact that a tool is necessary in order for producers to properly choose which upgrading technology will have the most benefit in terms of value and increased scrap utilization for their specific inputs and production portfolio. A batch planning model described in chapter 3 has been developed to perform this type of analysis; two case studies on specific technologies will be explored in the next section.

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

Technology	Ref	Capability	Use	Scrap	Form
Shredding	(Rousseau and Melin 1989)	Size reduction of any scrap stream	Wide industry use ~200 facilities in North America	All , but mainly automotive	Solid
Hand sorting	(Spencer 2005)	Capabilities vary, separate non-ferrous components from each other at best	Industry use concentrated in low labor cost regions	All	Solid
Magnetic sorting	(Wilson, Veasy et al. 1994)	Separate non-ferrous components from steel	Wide industry use	All	Solid
Air separation	(Veasey, Wilson et al. 1993)	Separate lighter weight materials (foams, plastics, rubber, etc.) out of non-ferrous scrap stream	Wide industry use	Non-ferrous scrap streams	Solid

Heavy media/sink-float	(Rousseau and Melin 1989)	Separate non-ferrous components from each other (Al, Mg, Cu, etc.)	Industry use ~10 facilities in North America	Non-ferrous, metallic scrap streams	Solid
Eddy current	(Kercher and Webb 1982; Schloemann 1982)	Separate metallic from non-metallic scraps	Wide industry use	All	Solid
Color ID/ Etching	(Wyss and Schultz 1999; Gesing, Stewart et al. 2000; Schultz and Wyss 2000)	Separate zinc, copper, brass, and stainless steel from aluminum, in conjunction with etching can separate Al by alloy family	Some industry use	Non-ferrous, metallic scrap stream	Solid
Spectrographic techniques	(Gesing, Stewart et al. 2001; Gesing, Torek et al. 2003; Gesing 2006)	Sort co-mingled streams by metal and alloy family, capability to sort by alloy in pilot plant stage	Small industry use, pilot plant scale	Co-mingled scrap stream	Solid
Hoopes process/ electrolytic	(Kamavaram, Mantha et al. 2003)	Removes Si, Fe, Mg, Mn, Cu, Zn, Cr	Industry use, small market	Low alloy content scraps	Liquid
Fractional crystallization	(Kahveci and Unal 2000; Sillekens, Schade Van Westrum et al. 2000)	Moves Si, Fe, Mg, Mn,	Pilot plant scale, R&D	High alloy content scraps	Liquid
Unidirectional solidification	(Kondo, Maeda et al. 1990)	Moves Si, Fe, Cu, Mg, Mn, Zn	Lab scale, R&D	High alloy content scraps	Solid
Distillation	(Ohtaki, Arakawa et al. 2000)	Removes Zn, Li from Al melt	Pilot plant scale, R&D	Aerospace alloy scraps	Liquid
Hot crush	(Ambrose, Brown et al. 1983; DeGaspari 1999)	Separate cast & wrought Al	Little industry use	Cast and wrought Al only scrap	Solid
Filters	(Frisvold, Engh et al. 1992; Oosumi,	Removes SiC, alumina inclusions	Wide industry use	All scrap melts	Liquid

	Nagakura et al. 2000)				
Flotation	(Veasey, Wilson et al. 1993)	Removes hydrogen	Wide industry use	All melts	Liquid
Fluxes	(Utigard, Friesen et al. 1998)	Prevent oxidation; remove gases, Ca, Sr, Na, Mg, Li, inclusions from Al melt	Pervasive industry use	Aluminum alloys	Liquid

Chapter 5. Evaluating upgrading technologies

As discussed in Chapter 1 and explored in detail in Chapter 4, there are a variety of solutions to deal with the negative impact on recycling of the accumulation of undesired elements or more broadly of the commingling of materials within secondary materials streams. Each of these strategies or technologies will have a trade-off between cost and scrap utilization (or recycling) as estimated by Figure 13. A variety of the technologies covered are still in the early stages of research and development and therefore their cost to be industrially implemented are not well characterized. Although qualitatively it is clear that such technologies could be useful, it is not clear that they would be economic and/or efficient. Understanding the cost and scrap utilization tradeoffs between these various strategies is critical to determining their value. The set of analytical tools described in the methods section was therefore implemented to quantify the potential value of scrap upgrading technologies, two specific cases will be presented: 1) dismantling and sorting of aerospace scrap, and 2) fractional crystallization.

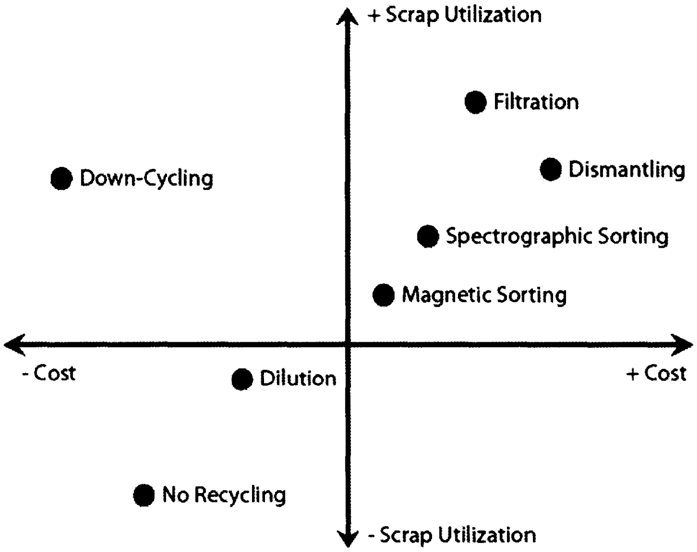


Figure 31. Possible cost and scrap utilization trade-offs of various strategies for dealing with compositional accumulation

5.1 Sorting and dismantling of aerospace scraps

5.1.1 Aerospace aluminum

Over the past few decades, the recycling rates of many aluminum products has not increased (cf. Figure 6). One sector that has received public scrutiny and which presents special challenges due to the use of special alloys is aerospace. Aerospace scraps may be a large resource, and relatively untapped compared to automotive. Boeing estimates that less than 60% of available aerospace materials are currently being recycled while the

Aircraft Fleet Recycling Association projects possible recycling rates of 90%(2008). This untapped resource for scrap aluminum is large; aluminum is *the* primary aircraft material, comprising about 80% of a plane's unladen weight(2006). It is used extensively for airframes, landing gear, engine components, propellers, and interior trim. A standard Boeing 747 jumbo jet, for example, contains approximately 75,000 kilograms of aluminum(2006). At an approximate rate of 300 per year, more than 6,000 civil aircraft are forecast to arrive at end-of-life in the next 20 years, potentially creating a large aerospace scrap market(Brown June 22, 2007). Many military aircraft are already available for possible scrap use, however, most are currently in storage at air force bases around the world(Veronico, Grantham et al. 2000). Other partially dissembled aircraft remain in aerospace "graveyards" (Figure 32); most of these are located in the southwestern United States as the dry conditions help to preserve the aluminum bodies and wings by preventing corrosion and rust. The under-utilization of these aerospace scrap materials indicates a lack of economic end-of-life options.

Figure 32. Boeing 707 nose and other parts in an airplane "graveyard" in the southwest United States. Photo by Telstar Logistics

Aircraft face a variety of fates at end-of-life; Figure 33 shows a few of these options schematically. Aircraft are often dismantled in order to re-sell or re-use whole parts in repairing other planes, however, this is associated with a high labor cost and low through-put(Horwitz 2007). Also, aerospace alloys are often riveted which provides unique challenges to clean dismantling. Another option is shredding the materials; this has a much lower cost but results in a co-mingled scrap stream. Many advantages exist for shredding aerospace scrap, the foremost being that a recycling infrastructure already exists due to the prevalence of automotive shredding and recycling facilities. Also, many aerospace companies closely guard the technologies present in their aircraft and therefore are hesitant to sell the plane in whole parts. Once the airplane is shredded, the scrap can remain as a co-mingled or mixed stream, or a sorting technology can be used to separate it.

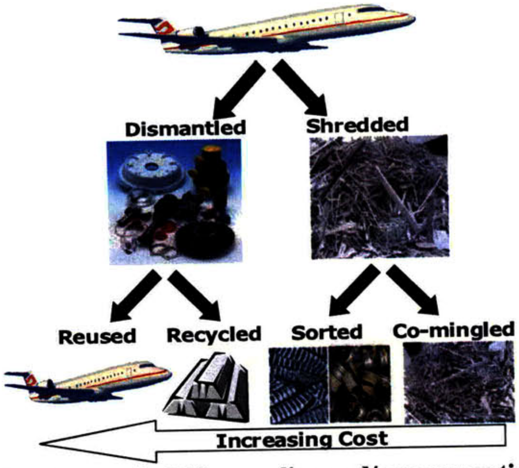


Figure 33. Schematic of various end-of-life recycling and/or reuse options for aerospace scrap

Table XVIII shows a list of typical aluminum alloys used in the airplane; one can see that the majority belong to the 2XXX and 7XXX series alloy families and therefore have high copper and zinc alloying levels, respectively. Shredded or co-mingled aerospace scrap will therefore be a mix of these alloys and also often have a high degree of compositional uncertainty. The high levels of copper and zinc limit the amount of aerospace scrap that can be re-used in new aluminum production. To make use of a shredded or co-mingled aerospace scrap stream, the composition will likely require upgrading. The use of laser based sorting technologies has been suggested(Das and Kaufman 2007; Gesing and Harbeck 2008) to provide more opportunities for usage of these scraps.

Table XVIII. Typical aerospace alloys, reproduced from (Gesing and Harbeck 2008)

Alloy Family	Alloy	Application
Al + Cu	2X14, 2X19, 2X24	sheet and plate
	2014, 2X18, 2024, 2026	extrusions
Al + Zn	7010, 7X50, 7X75	sheet and plate
	7X50, 7055, 7X75	extrusions, sheet
Al + Li	2050, 2X95, 2090, 2X98	sheet and plate
	2X96, 2099	extrusions
Al + Mg	5086	sheet
Al + Mg + Si	6056, 6061	extrusions
	6061	sheet and plate
Mg + Al + RE	AE41, AE44	creep-resistant castings

5.1.2 Laser based sorting technologies for aerospace

Laser induced breakdown spectroscopy (LIBS) was first developed by Los Alamos National Laboratory; its first application to composition identification of metallic scrap pieces was in 1990 in a joint project with Metallgesellschaft, formerly a large mining and engineering company based in Germany(Sattler 1990; Sattler and Yoshida 1993). In this method, a sensor detects a piece of scrap material which activates a pulse laser. The laser hits the surface of the metal and produces an atomic emission. The optical spectra are read by a polychromator and a photodiode detector which sends a signal to a computer system(Gesing, Stewart et al. 2001). The system can then direct the piece of scrap to an appropriate bin using a mechanical arm. Another system under development utilizes an air table; the detector sends a signal which triggers a burst of air beneath the scrap metal thus ejecting it into the correct container. LIBS has many advantages over current separation technologies for both automotive and aerospace applications as it has the possibility for high speed and high volume. It has capabilities to separate wrought and cast alloys as well as sort wrought alloys by alloy family(Gesing, Berry et al. 2002; Gesing, AuBuchon et al. 2003). Some drawbacks to commercial use remain however. Pulse lasers can only penetrate a small distance into the surface of a metal and therefore, the scrap must be free of lubricants, paint, and other coatings. Even when the scrap is clear of these, oxide formation on the surface could cause erroneous readings. While this technology is starting to gain ground in automotive applications, its use for sorting aerospace scraps has not been documented. LIBS's capabilities combined with the compositional characteristics of aerospace scrap (mixed 2XXX and 7XXX alloys), however, indicate possible cost savings for its application.

5.1.3 Case details

A hypothetical aluminum secondary production case study was devised to test the consequences of various end-of-life aerospace processing decisions on production cost and scrap utilization. Fifteen finished alloys were chosen to represent a broad production portfolio including both aerospace applications as well as other major products such as automotive and packaging. They are listed with their maximum and minimum compositional constraints in Table XIX; these specifications are based on guidelines set by the Aluminum Association and do not reflect production targets of any specific firm. It was assumed that an equal amount of each would be produced.

Scrap compositions were based on the three end-of-life processing scenarios: dismantled, sorted, and co-mingled as indicated in Figure 33. Reuse of dismantled pieces will be neglected as this would occur outside of the aluminum secondary industry. For the

dismantled case, it was assumed the scrap composition would be an average of the AA specification for eight of the major alloys used in aircraft(Das and Kaufman 2007) with four each for 2XXX and 7XXX series alloys. It was assumed that the **sorting** technology employed would have the capability to separate a mixed, shredded scrap stream into individual series. Therefore, the composition for these scraps was assumed to be a series average of the dismantled case compositions. For the **co-mingled** case, it was assumed these compositions would be a total average of the eight major alloys represented in the dismantled case; these compositions are given in Table XX. For all three cases, actual scrap composition would likely vary from the specific assumptions used. Scrap composition is inherently uncertain as described in previous chapters, also, these cases are a simplification of the alloys present in a typical aircraft. Economic evaluation of any specific technology will require actual characterization of available aerospace scrap. Prices for primary aluminum and alloying elements were taken from USGS 2005 averages(Kelly, Buckingham et al. 2004) while scrap prices were assumed to be at a 50% discount to primary aluminum. All raw materials were assumed to be unlimited in availability to avoid the potential effects of limited raw materials supplies. For the base case, the incoming scraps were modeled with a coefficient of variation of 15% on composition for all elements. The coefficient of variation is the standard deviation normalized by the mean as shown in Equation (5.1). Sensitivities around this number were explored.

$$COV = \frac{\sigma}{\mu} \qquad (5.1)$$

Table XIX. Maximum and minimum compositional specifications for finished alloys in weight fraction(Gesing 2001)

Alloys		Si Max	Si Min	Mg Max	Mg Min	Fe Max	Fe Min	Cu Max	Cu Min	Mn Max	Mn Min	Zn Max	Zn Min
Aerospace	2014	0.012	0.005	0.008	0.002	0.007	0	0.05	0.039	0.012	0.004	0.0025	0
	2024	0.005	0	0.018	0.012	0.005	0	0.049	0.038	0.009	0.003	0.0025	0
	7075	0.004	0	0.029	0.021	0.005	0	0.02	0.012	0.003	0	0.061	0.051
	7178	0.004	0	0.031	0.024	0.005	0	0.024	0.016	0.003	0	0.073	0.063
Castings	319	0.065	0.055	0.001	0	0.01	0	0.04	0.03	0.005	0	0.01	0
	356	0.075	0.065	0.004	0.002	0.006	0	0.0025	0	0.004	0	0.0035	0
	356	0.075	0.065	0.004	0.002	0.002	0	0.002	0	0.001	0	0.001	0
	381	0.095	0.075	0.001	0	0.02	0	0.04	0.03	0.005	0	0.03	0
Bumpers	7003	0.003	0	0.01	0.005	0.004	0	0.002	0	0.003	0	0.065	0.05
	7129	0.002	0	0.02	0.013	0.003	0	0.009	0.005	0.001	0	0.052	0.042
Auto	2036	0.005	0	0.006	0.003	0.005	0	0.03	0.022	0.004	0.001	0.0025	0
	6061	0.008	0.004	0.012	0.008	0.007	0	0.004	0.002	0.002	0	0.0025	0
Can stock	3004	0.003	0	0.013	0.008	0.007	0	0.0025	0	0.015	0.01	0.0025	0
	3104	0.006	0	0.013	0.008	0.008	0	0.0025	0.001	0.014	0.008	0.0025	0
	3105	0.006	0	0.008	0.002	0.007	0	0.003	0	0.008	0.003	0.004	0

Table XX. Average potential compositions for scraps in weight fraction

Cases	Alloys	Si	Mg	Fe	Cu	Mn	Zn
Dismantled	2014	0.0085	0.005	0.0035	0.0445	0.008	0.00125
	2214	0.0085	0.005	0.0015	0.0445	0.008	0.00125
	2024	0.0025	0.015	0.0025	0.0435	0.006	0.00125
	2324	0.0005	0.015	0.0006	0.041	0.006	0.00125
	7050	0.0006	0.0225	0.00075	0.023	0.0005	0.062
	7075	0.002	0.025	0.0025	0.016	0.0015	0.056
	7475	0.0005	0.0225	0.0006	0.0155	0.0003	0.057
	7178	0.002	0.0275	0.0025	0.02	0.0015	0.068
Sorted	2XXX	0.005	0.01	0.002025	0.043375	0.007	0.00125
	7XXX	0.001275	0.024375	0.001588	0.018625	0.00095	0.06075
Co-mingled	Mixed	0.003138	0.017188	0.001806	0.031	0.003975	0.031

5.1.4 Results

Comparison of scrap utilization (left axis, bars) and production cost in $/kt (right axis, diamonds) for each of the three aerospace end-of-life cases, dismantled, sorted and co-mingled, is shown in Figure 34, assuming 15% COV on the scrap streams' composition. The dismantled case has the highest scrap utilization and therefore, lowest total production cost; it provides savings of 24% compared to producing the finished alloy portfolio using no scrap materials (Table XXI). The sorted case provides lower utilization and cost savings than the dismantled case; however, it still significantly outperforms the co-mingled case by 22%. This would suggest that much value can be gained from upgrading of shredded aerospace scrap as opposed to simply leaving it co-mingled. These cost savings, however, will be reduced by the actual expense of the upgrading technology in question. Producers and recyclers can make use of this framework to evaluate their specific technologies.

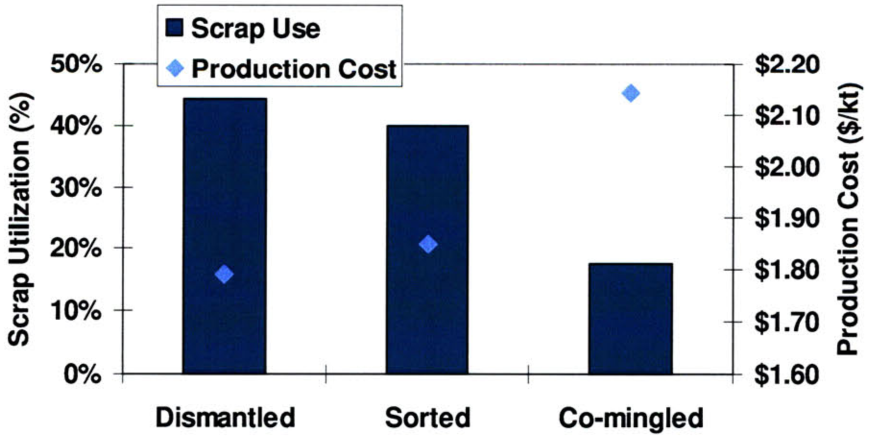


Figure 34. Base case scrap usage and production cost for the dismantled, sorted and co-mingled end-of-life cases assuming no compositional uncertainty

Table XXI. Cost savings compared to a no scrap case for end-of-life cases assuming no compositional uncertainty

Case	ΔCost ($/kt)	Cost Savings
Dismantled	$0.575	24%
Sorted	$0.518	22%
Co-mingled	$0.227	10%

Examining these base case results in more detail, Figure 35 shows how the scrap utilization is broken down between the alloys in the production portfolio. As one would expect, the aerospace alloys are able to use the most of these scraps for all three end-of-life cases due to the close compositional matching between the scraps and products. However, the aerospace industry is extremely conservative in their scrap utilization due to the strict standards for meeting specifications (cf. aerospace in Table XIX). If aerospace scraps are to be used in greater quantity, other large markets would have to be available.

Quite surprising is the extremely low utilization of these scrap streams by cast alloys. Castings are generally the most forgiving alloys in terms of scrap use due to their large specification windows, especially in terms of silicon and iron (cf. Table XIV). However, the high zinc and copper alloying element amounts present in aerospace scraps, even when dismantled, prevent their usage in castings. Can stock, a product that typically contains recycled content percentages >80%, also shows surprisingly low utilization for aerospace. Aluminum alloys used to produce automotive bumpers are typically 7XXX series alloys and can therefore consume scrap with high zinc levels. Though the total amount of scraps used in castings is small compared to the other products, the production of 380, 319 and 356 cast alloy variants made up 41% of the net product shipments by independent smelters in the United States in 2006, or roughly 309,000 metric tons of aluminum(Kelly and Matos 2006). Wrought extrusions, of which 6061, bumper sheet, and can sheet would be included, made up nearly 40% of net product shipments as well, or roughly 301,000 metric tons of aluminum. So while the utilization for these products is fairly low (<30% for even the dismantled case); these large markets may still provide a significant sink for recycled aerospace.

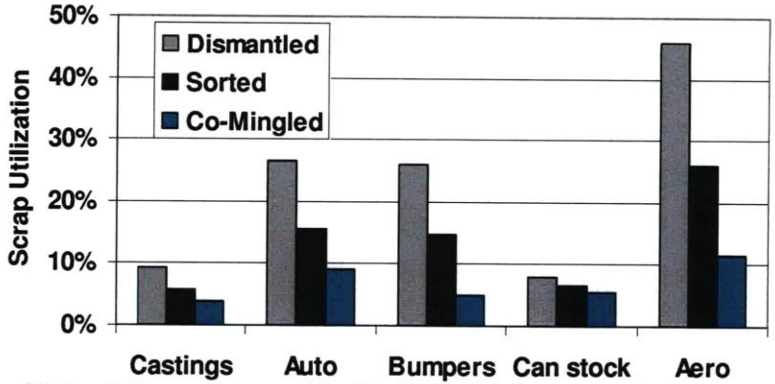
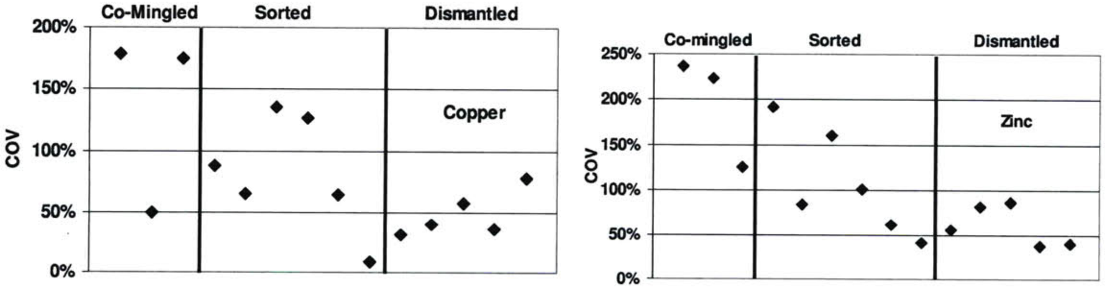


Figure 35. Breakdown of scrap utilization by product category for base case results

5.1.5 Sensitivity analysis: compositional uncertainty

In reality, some degree of compositional uncertainty exists in the recycled scrap streams. The coefficient of variation (COV, standard deviation normalized by the mean) can be a quantitative measure of this degree of compositional uncertainty. Looking at variations in real scrap streams using data from a large secondary producer, specifically for zinc and copper, shows the wide range in these values (Figure 36). The magnitude of this number is difficult to estimate a priori for scraps in general and particularly for aerospace scraps as it will depend on the efficiency of end-of-life processing and the compositional element in question. Qualitatively, one would expect the highest degree of uncertainty in the co-mingled scrap stream, followed by the sorted stream, and with the lowest uncertainty in the dismantled case. This is generally reflected in Figure 36.



A)

B)

Figure 36. Actual coefficient of variation data for fourteen different scrap streams for a) copper and b) zinc showing a wide range in values.

Using a chance-constrained blending model, as described in section 3.1.2, allows for sensitivity analysis to be performed on the compositional uncertainty or COV of the resulting scrap stream. This sensitivity is important because the accuracy of these technologies is unknown. Figure 37 shows how the total scrap utilization would be expected to change with increasing compositional uncertainty (higher coefficient of variation). The change in total production cost compared to a case using no recycled materials is shown in Figure 38. The scrap utilization and cost for the sorted case (gray squares) change sharply and adversely at 20% COV. This implies that if the sorting technology has a low efficiency, it may not provide enough improvement over the co-mingled case to be worthwhile. This will of course depend on the costs, including development, equipment, and tooling, associated with the specific sorting technology. The dismantled case (black diamonds) provides significant cost savings up to coefficients of variation of ~60%. However, it is unlikely that dismantled scraps would have such high compositional uncertainty; more realistic would be COV's less than 20%. The trade-off between the cost savings provided by dismantling and the high labor cost would need to be analyzed in order to determine the value of this end-of-life option.

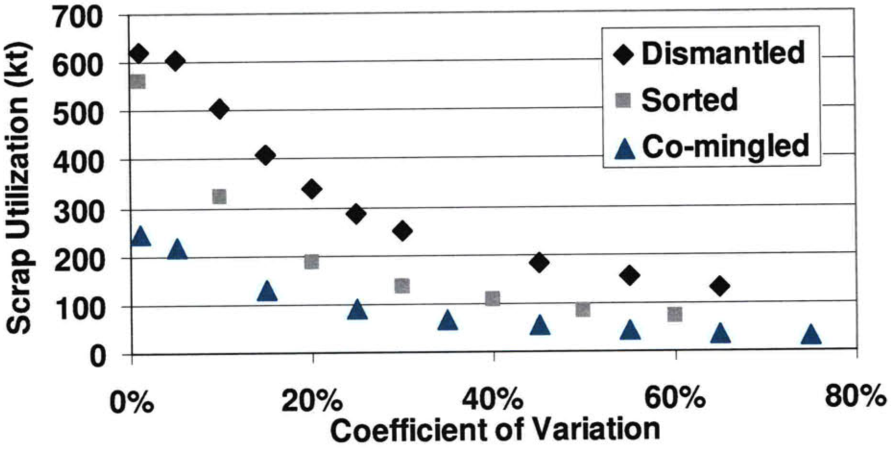


Figure 37. Change in scrap utilization with increasing compositional uncertainty for each of three end-of-life recycling cases

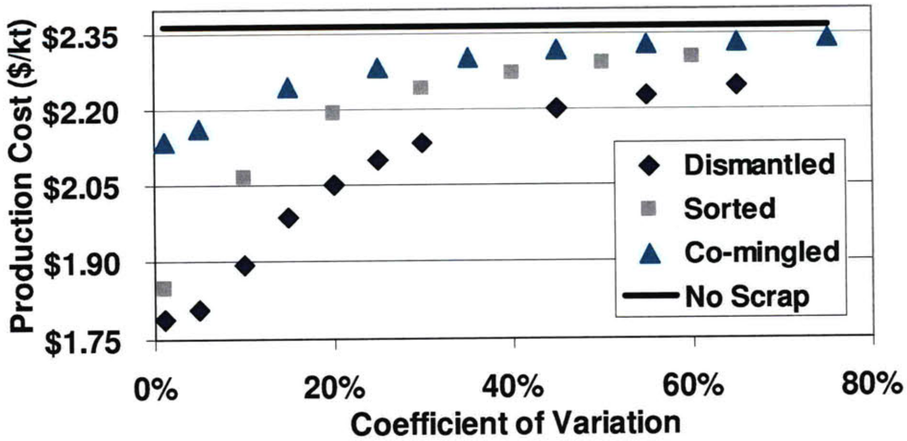


Figure 38. Change in production cost with increasing compositional uncertainty for each of three end-of-life recycling cases as well as the case where no scrap is utilized

As stated previously, it would be assumed that the compositional COV for the dismantled case would be less than the sorted case which would be less than the co-mingled case ($COV_{dismantled}<COV_{sorted}<COV_{co\text{-}mingled}$). Assuming various compositional uncertainties that may be more appropriate for each of the end-of-life scenarios, the base case results for scrap utilization were reproduced. A coefficient of variation of 15% was assumed for dismantled scraps, 30% for the sorted case, and 65% for the co-mingled scrap stream. The effect on the overall cost savings for this case is shown in Table XXII as the last row of values (varying COV). The change in the base case results assuming an equal amount of uncertainty (15% COV) assumed for each scenario is also shown. The effect of having varying COV's on the breakdown of utilization by product category is shown in Figure 39.

Table XXII. Cost savings (compared to no scrap use) for cases with varying COV

	Dismantled	Sorted	Co-Mingled
No uncertainty	24%	22%	10%
All 15% COV	16%	13%	5%
Varying COV case	16%	5%	1%

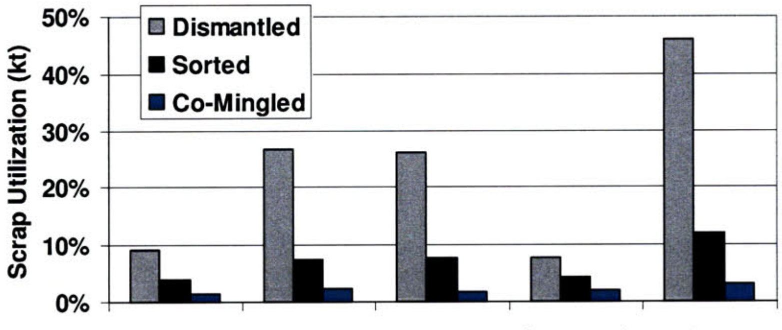


Figure 39. Breakdown of scrap utilization by product category assuming compositional uncertainty for each of the end-of-life scenarios (Dismantled COV = 15%, Sorted = 30%, Co-mingled = 65%)

5.1.6 Sensitivity analysis: shadow prices

The results of a linear optimization problem are a set of decision variables that give the optimal objective function. In the case of secondary alloy production planning, these decision variables are the amounts of scrap and primary raw materials to be purchased. However, linear optimization solutions also provide a powerful set of information that quantifies the sensitivity of these results to changes in assumptions. These sensitivity parameters are known as "shadow prices". Specifically, a shadow price is the change in the objective function at the optimum when a specific constraint is changed by one unit(Neufville 1990) as expressed in Equation (5.2). Each shadow price has a range of validity associated with it. Interested readers should consult (Cosquer 2003; Cosquer and

Kirchain 2003) for a lengthier discussion on the value of this information for decision-makers.

$$SP_{\text{Constraint}} = \frac{\delta(\text{Production Cost})}{\delta(\text{Constraint})} \tag{5.2}$$

As has been shown previously(Gaustad, Li et al. 2006), compositional constraints have one of the largest effects on the optimized scrap use and production cost. The magnitude and sign of these shadow prices indicates how the production cost would change if the compositional specifications were tightened or loosened. For the upgrading cases presented here, there are a total of 180 compositional constraints (15 products * 6 tracked elements * 2 specifications, one for the maximum and one for the minimum). For each of the three end-of-life cases, approximately half of these are binding. It is no surprise that more of the binding constraints are maximums (Table XXIII); specifically 55-61 out of 180 or 66-72% of the binding constraints. The amount of contaminants in a scrap usually determines how much dilution with primary aluminum is required and is therefore the major limiting factor. The shadow prices on magnesium, copper, and manganese are typically higher because these three alloying elements are the most expensive (>$2/kiloton) and therefore have the highest impact on the production cost.

As shown in Table XXIII, out of the top thirty binding compositional constraints, zinc and copper constraints make up the vast majority for the dismantled and sorted cases (90% and 93% respectively) and a large portion for the co-mingled case (53% total). Previous studies(Das and Kaufman 2007) have hypothesized that high copper and zinc levels are one of the key barriers to higher utilization for aerospace scraps. This is certainly the case, and interestingly, for the sorted and dismantled cases, copper and zinc remain the most constraining elements. Though both of these end-of-life processes allow for increased usage of the aerospace scrap, the high amount of copper and zinc is still the limiting factor.

Table XXIII. Compositional shadow prices; number that are binding, maximums, zinc and copper

	Dismantled	Sorted	Co-mingled
Total Constraints	180	180	180
Binding	85	89	83
	47%	49%	46%
Maximums	61	60	55
	72%	67%	66%
Copper (top 30)	16	19	11
	53%	63%	37%
Zinc (top 30)	11	9	5
	37%	30%	17%
Cu & Zn Total	90%	93%	53%

5.1.7 Discussion

End-of-life aerospace materials remain a comparatively untapped source of valuable aluminum scrap. Using an optimization model for batch mixing decisions has shown that upgrading, specifically dismantling and sorting, can provide cost savings through increased aerospace scrap utilization when compared to shredding (co-mingled scrap stream). This improvement was shown to be heavily dependent on the post-processing amount of uncertainty in the scrap composition and therefore the efficiency and accuracy of the technology in question. For example, the sorted case would need to have compositional coefficients of variation less than 20% to provide significant savings over the co-mingled case. In the end, a final conclusion on these technologies would require more precise quantification of the characteristics of end-of-life aerospace scrap and complementary information on the expected costs of the various technologies.

5.2 Evaluating fractional crystallization

5.2.1 The fractional crystallization process

The fractional crystallization refining process is typically used to remove impurities from primary aluminum in order to produce very high purity aluminum (>99.97% or 3N7). Fractional crystallization provides cost savings compared to both three-layer electrolytic refining and zone refining(Kahveci and Unal 2000). The Alcoa fractional crystallization method has been shown to produce aluminum of 3N7 to 6N quality; typical applications include memory disks, capacitor foil, and other electronic applications(Kahveci and Unal 2000). However, in recent years, this technology has been extended to refining scraps; in Kahveci and Unal's study(Kahveci and Unal 2000) a 5XXX series scrap material was tested.

In the fractional crystallization process, the melt surface is cooled rapidly in order to form aluminum crystals. These purified crystals settle to the bottom of the furnace and the remaining liquid continues to accumulate impurities. The remaining liquid aluminum (containing high levels of impurities) is removed from the furnace first; this material is referred to as the "downgrade". The purified crystals left in the bottom of the furnace are then re-melted and removed; this material is referred to as the "upgrade". This process can be done in multiple refining steps as illustrated schematically in Figure 40.

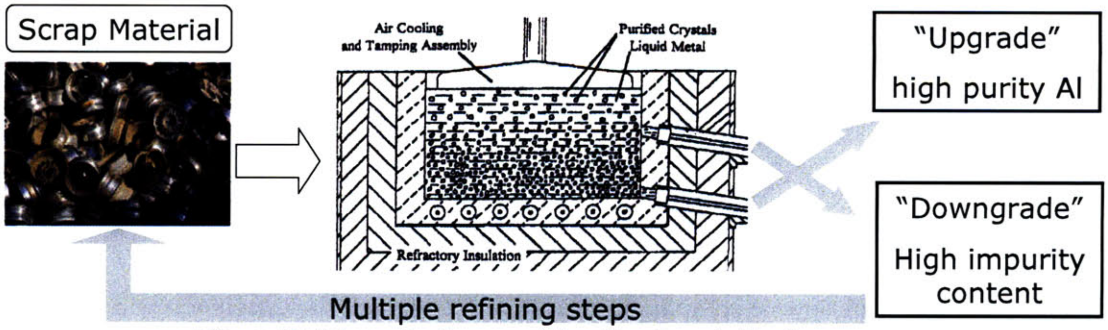


Figure 40. Schematic diagram of fractional crystallization process

This technology takes advantage of the thermodynamic behavior of dilute eutectic binary systems; specifically, that above the eutectic temperature the solute material will be present in the liquid while the solid that forms will be high purity aluminum. One can estimate the degree to which an element can be removed by examining the binary phase diagram and calculating the thermodynamic or equilibrium distribution coefficient. In the literature, equilibrium distribution coefficients are calculated in two ways as either 1) the ratio of the solute concentration in the solid to the solute concentration in the liquid, or 2) the ratio of the solute concentration in the solid to the original concentration of the solute. The values as calculated according to Equations (5.3) from two studies, one at Alcoa(Kahveci and Unal 2000) and one at Delft(Sillekens, Schade Van Westrum et al. 2000), are reported in Table XXIV. Elements that form a peritectic in the aluminum binary phase diagram will have equilibrium distribution coefficient great than one (Cr, V, Zr, Ti) and will therefore accumulate in the upgraded portion of the melt. Therefore, these impurities must be removed from the melt before the refining process; this is typically accomplished using boride formation. The lower the distribution coefficient, the more that impurity will partition in the liquid and therefore more of it can be removed from the upgraded portion. For example, Fe, Ni, and Si can be almost wholly removed from the purified aluminum stream while Mn and Zn will remain in a higher concentration.

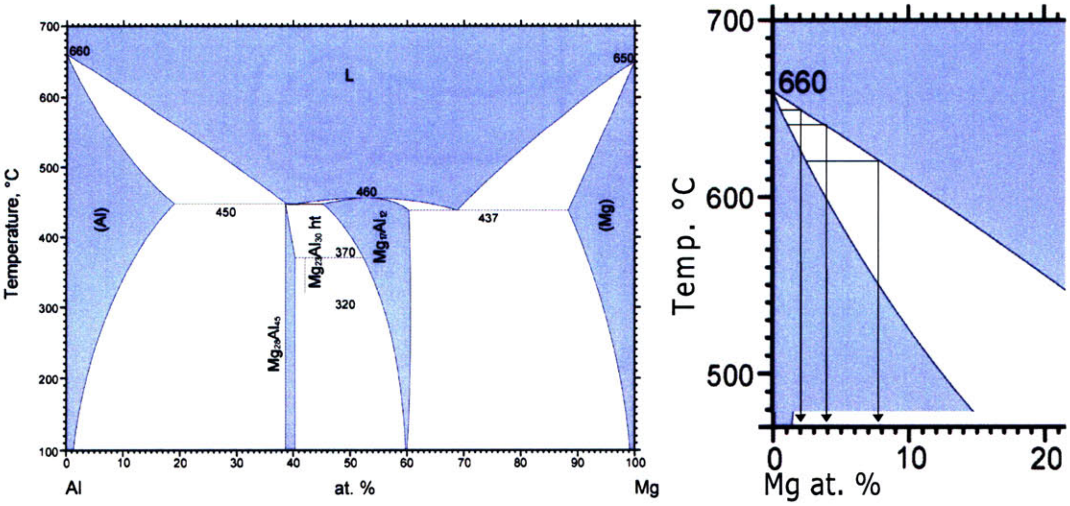
$$\text{Alcoa } k = \frac{c_{\text{solute in solid}}}{c_{\text{solute in liquid}}} \quad \text{Delft } k = \frac{c_{\text{solute in solid}}}{c_{\text{solute original}}} \tag{5.3}$$

Table XXIV. Equilibrium distribution coefficients as calculated by the Alcoa(Kahveci and Unal 2000) and Delft(Sillekens, Schade Van Westrum et al. 2000) studies (*= estimated and not calculated for the Delft study, X=not provided by Delft study)

	Alcoa	Delft
Sn	0.001	0*
Fe	0.03	0.03
B	0.045	X
Ni	0.008	0
Si	0.1	0.13

Cu	0.14	0.17
Ga	0.2	0.20*
Mg	0.25	0.45*
Zn	0.5	0.87*
Mn	0.93	0.62
Cr	1.9	X
V	2.4	X
Zr	2.55	X
Ti	6.7	X

To illustrate how these coefficients were determined as well as the large range in their magnitude, two examples were calculated from binary phase diagrams: magnesium and copper. The initial impurity concentration and the holding temperature for the process were not reported in either case study so a range of values was used. It was assumed that the temperature used for the calculation was quite close to the melting temperature of aluminum so 650°C, 640°C and 620°C were used. For the case of magnesium, there was a large difference between the Alcoa and Delft coefficients (0.25 and 0.45 respectively). Figure 41A shows the full Al-Mg binary phase diagram and Figure 41B expands this diagram to the area of interest; using the lever rule at the temperatures cited above, one can project the concentrations in the solid and liquid portions within this region (Figure 41). The equilibrium distribution coefficients can then be calculated according to Equation (5.3) and are shown for varying initial Mg concentration and holding temperatures in Figure 42. To match the study data, one could then deduce that the initial magnesium concentration for the tested scrap materials was less than 1wt.% at 650°C, 1-2 wt.% at 640°C, and between 2-4 wt.% at 620°C.



A) B)

Figure 41. A) Binary phase diagram for Al-Mg system and B) close-up of liquid-solidus area below the aluminum melting temperature © ASM International 2006. Diagram No. 900102

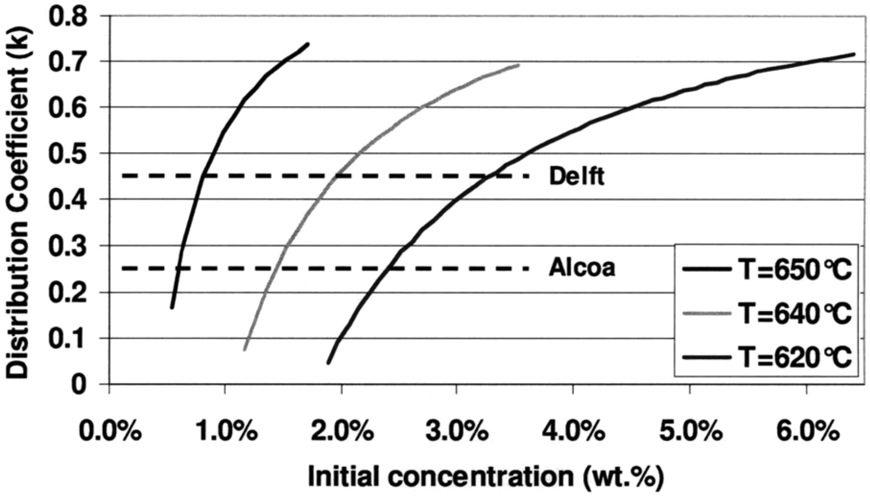


Figure 42. Calculated magnesium equilibrium distribution coefficients for varying initial concentrations and holding temperatures compared to reported values from Alcoa study (0.25) and Delft study (0.45)

For the case of copper, there is much closer agreement between the values calculated in the Alcoa and Delft studies. Similarly to above, the lever rule can be used for the Al-Cu binary phase diagram (Figure 43) and the resulting coefficients plotted for varying initial copper impurity concentrations as shown in Figure 44 and Figure 45. These two figures show how the coefficients vary when using the different k formulations listed in Equation (5.3). To match the Alcoa study data, one would use Figure 44 and deduce that the initial copper concentration for the tested scrap materials was 1.2 wt.% at 650°C, 2.2 wt.% at 640°C, and 5 wt.% at 620°C. For the Delft study, Figure 45 shows that the initial copper concentration was likely 1 wt.% at 650°C, 2 wt.% at 640°C, and 4.2 wt.% at 620°C.

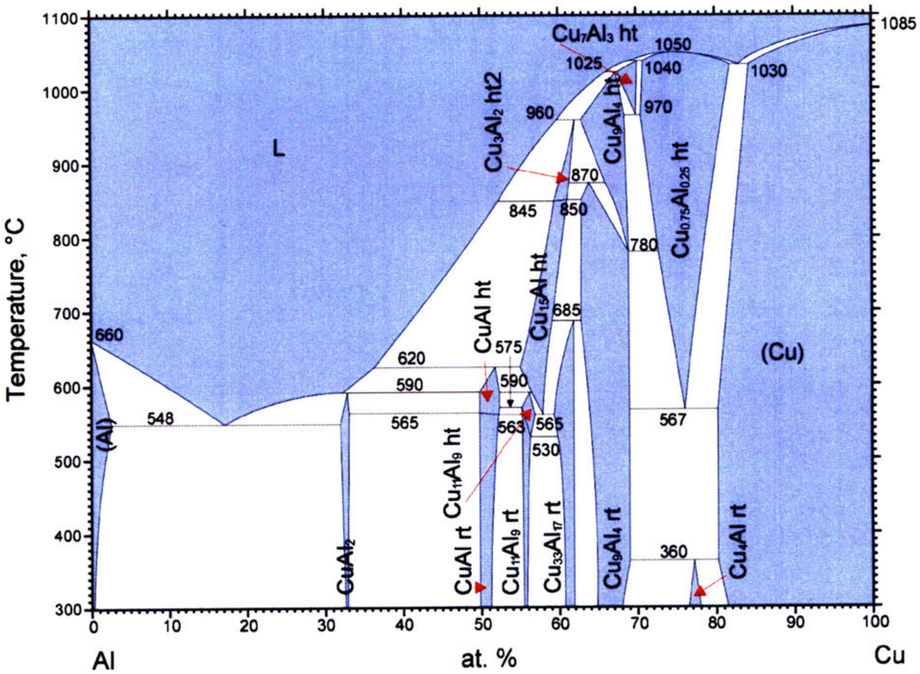


Figure 43. Binary phase diagram for Al-Cu system © ASM International 2006. Diagram No. 900085

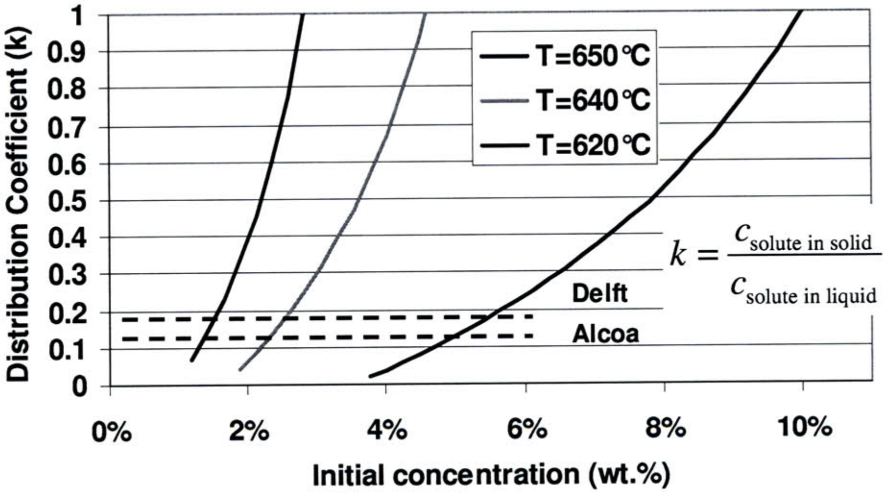


Figure 44. Copper equilibrium distribution coefficients calculated by the Alcoa method for varying initial concentrations and holding temperatures compared to reported values from Alcoa study (0.15) and Delft study (0.17)

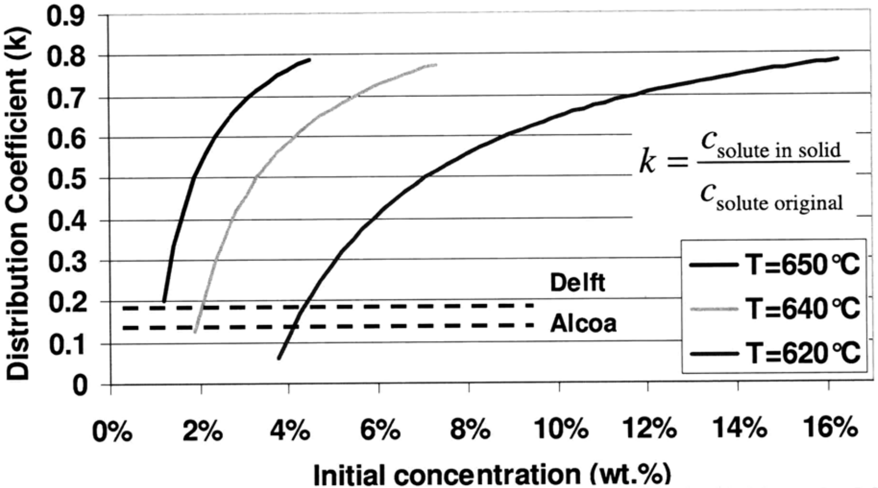


Figure 45. Copper equilibrium distribution coefficients calculated by the Delft method for varying initial concentrations and holding temperatures compared to reported values from Alcoa study (0.15) and Delft study (0.17)

Examining these coefficient calculations in more detail highlights the uncertainty surrounding their values. This uncertainty motivates the need for a method that can perform sensitivity analysis surrounding the composition of these upgraded scrap streams. The chance-constrained batch planning model described in chapter 3 and used for the previous case provides this capability.

5.2.2 Case details

A hypothetical production portfolio was devised in order to test under what conditions the resulting compositional changes of the fractional crystallization process could provide increased scrap usage and cost savings. Twenty alloys were chosen as the finished alloy portfolio representing a broad range of allowable impurity levels with production of 100 kt each. These included applications requiring high purity such as electrolytic capacitor foil and disk blanks, medium purity applications such as aerospace alloys, as well as applications requiring lower purity aluminum such as castings, automotive, and packaging alloys. This production portfolio and each alloy's maximum and minimum compositional constraints are listed in Table XXV. The electrolytic capacitor foil (ECF) and disk blank (DB) specifications are based on industry targets(Marubeni 2007) while all other alloys are based on Aluminum Association specifications. Prices for primary aluminum and alloying elements were taken from USGS 2005 averages(Kelly, Buckingham et al. 2004). The varying compositions for the input scrap materials, both downgrade and upgrade, were used directly as reported in (Kahveci and Unal 2000). A total initial amount of scrap material of 100 kt was assumed; for example, if the upgrade yield was 80%, this would correspond to 80 kt of upgraded material and 20 kt of downgraded material.

Table XXV. Compositional specification for the production portfolio including both high purity and low purity applications

	Si		Mg		Fe		Cu		Mn		Zn	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
ECF1	0.006	0	0.000001	0	0.007	0	0.0015	0	0.011	0	0.000001	0
ECF2	0.006	0	0.000001	0	0.007	0	0.0009	0	0.013	0	0.000001	0
1050	0.0025	0	0.0005	0	0.004	0	0.0005	0	0.0005	0	0.0005	0
1060	0.0025	0	0.0003	0	0.0035	0	0.0005	0	0.0003	0	0.0005	0
3003	0.006	0	0.000001	0	0.007	0	0.002	0.0005	0.015	0.01	0.001	0
8011	0.009	0.005	0.0005	0	0.01	0.006	0.001	0	0.002	0	0.001	0
DB-1	0.004	0	0.045	0.035	0.005	0	0.001	0	0.007	0.002	0.0025	0
DB-2	0.0004	0	0.045	0.035	0.0005	0	0.0009	0.0003	0.0005	0	0.002	0.001
DB-3	0.001	0	0.045	0.035	0.0016	0	0.0003	0	0.007	0.002	0.0005	0
DB-4	0.0003	0	0.05	0.04	0.0002	0	0.0002	0	0.0003	0	0.0002	0
2014	0.0120	0.0050	0.0080	0.0020	0.0070	0.0000	0.0500	0.0390	0.0120	0.0040	0.0025	0.0000
4045	0.1100	0.0900	0.0005	0.0000	0.0080	0.0000	0.0030	0.0000	0.0005	0.0000	0.0010	0.0000
6063	0.0060	0.0020	0.0090	0.0045	0.0035	0.0000	0.0010	0.0000	0.0010	0.0000	0.0010	0.0000
7005	0.0035	0.0000	0.0180	0.0100	0.0040	0.0000	0.0010	0.0000	0.0070	0.0020	0.0500	0.0400
3004	0.0030	0.0000	0.0130	0.0080	0.0070	0.0000	0.0025	0.0000	0.0150	0.0100	0.0025	0.0000
5052	0.0025	0.0000	0.0280	0.0220	0.0040	0.0000	0.0010	0.0000	0.0010	0.0000	0.0010	0.0000
6061	0.0080	0.0040	0.0120	0.0080	0.0070	0.0000	0.0040	0.0015	0.0015	0.0000	0.0025	0.0000
319	0.065	0.055	0.001	0	0.01	0	0.04	0.03	0.005	0	0.01	0
356	0.075	0.065	0.004	0.002	0.006	0	0.0025	0	0.0035	0	0.0035	0
380	0.095	0.075	0.001	0	0.02	0	0.04	0.03	0.005	0	0.03	0

5.2.3 Base case results

For the fractional crystallization study described in (Kahveci and Unal 2000), a 5XXX series scrap was refined. As the refining progresses, part of the melt becomes purified (the upgrade) while the removed impurities accumulate in the rest of the melt (the downgrade). Figure 46 shows the modeled scrap usage (left axis) of both the upgraded and downgraded material and production cost (right axis) at several snapshots of the fractional crystallization process. The upgrade yield refers to the amount of crystallized material in the melt with 0% being the starting point of refining, where no upgrading has occurred. For this case, one can see that all of the upgrade and downgrade are utilized at each refining step. The result is a minimum in the production cost corresponding to approximately 25% yield. This means that the highest cost savings of purification by fractional crystallization are realized early on in the refining process. While the actual costs of this upgrading technology are not known by the authors, producers can make use of these results to understand the scrap use and economic trade-offs of the process.

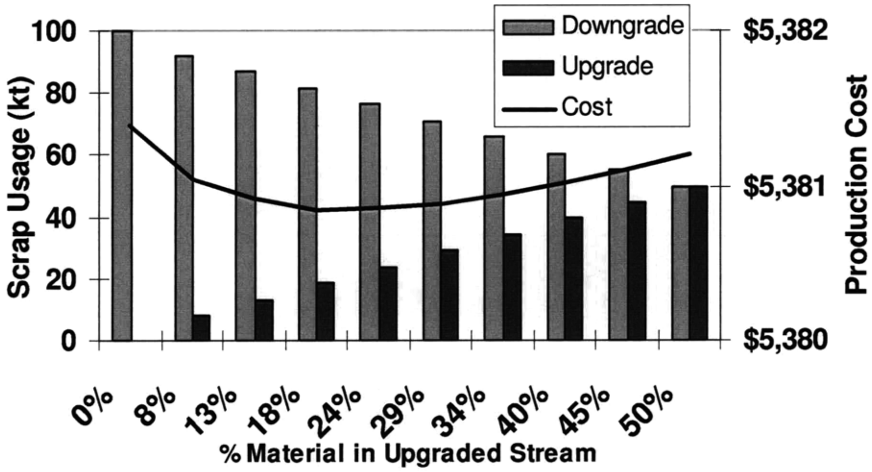


Figure 46. Amount of upgrade and downgrade scrap utilization and total production cost for various stages of the refining process, represented by the percentage of upgrade yielded in the melt

Before performing this analysis, one might assume that increased purification would reduce costs by increasing scrap utilized in the "high technology" or tighter specification products. However, Figure 47 shows that the degree of refining does not correlate to the high tech utilization. Though the overall cost savings may seem quite small (only 3.6% of the overall production cost), examining four specific alloys show individual cost savings as high as 27% (Figure 48). Interestingly, not all the alloys produced have their maximum cost savings at 25% upgrade yield. This large range in benefits would lead one to ask under what conditions are scrap utilization and cost savings maximized? The sensitivity analysis in the following section will attempt to answer this question.

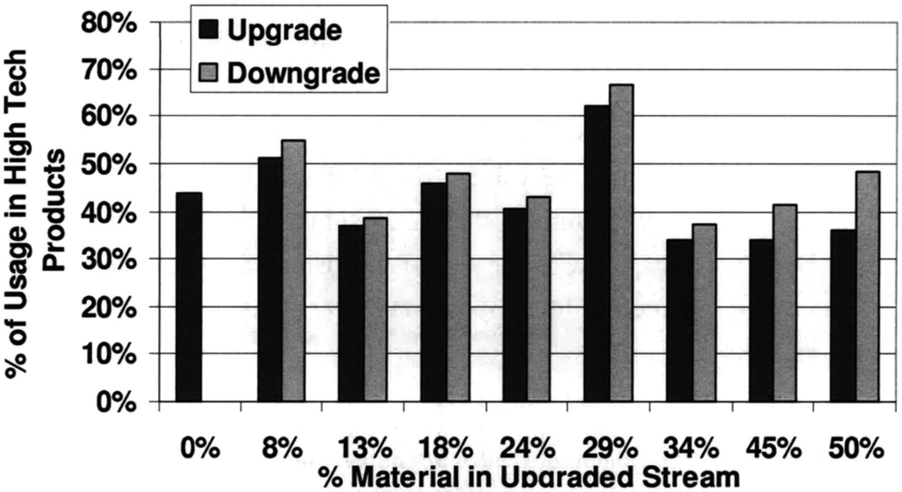


Figure 47. Breakdown of upgrade and downgrade usage in high tech products (as % of total utilization)

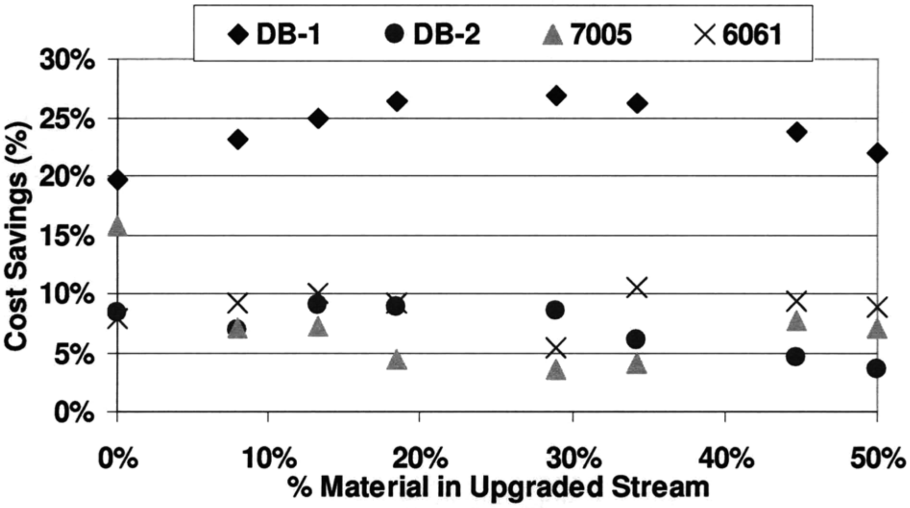


Figure 48. Individual cost savings for two high purity alloys for disk blanks and two lower purity alloys (6061 and 7005)

5.2.4 Sensitivity analysis: extension to other scrap types

While the base case results are informative as to the economic and environmental possibilities of the fractional crystallization process, they are for the specific case of refining a 5XXX series scrap. These scraps are quite high in Mg which has neither the highest nor lowest distribution coefficients for removal. As derived in (Sillekens, Schade Van Westrum et al. 2000), the equilibrium distribution coefficients are the ratio of the solute concentration in the solid to the solute concentration in the liquid determined from the binary phase diagram for aluminum and each of the impurities. It would be quite useful for producers to know how the cost savings trend would shift for this particular upgrading technology if other types of scraps are to be refined.

Using the analysis in (Kahveci and Unal 2000), compositional multipliers for each element at several stages (or upgrade yield levels) were estimated (Table XXVI). From these multipliers, one can see that Si has the highest potential for removal from the melt and Mn has the lowest. One would then hypothesize that the cost savings for scraps high in Si could be much larger than the values found for the base case scrap. To test this hypothesis, three secondary materials that are common on the scrap market were selected: used beverage cans (UBC), alloy 6061 extrusion scrap, and automotive casting scraps. A less common, but close in composition to the base case 5XXX series scrap was also tested (alloy 5184).

Table XXVI. Multiplier for upgrade (up) and downgrade (down) composition at various refining "snapshots" represented by the amount of yielded upgrade in the melt(Kahveci and Unal 2000)

	50%		60%		70%		80%		90%	
	Up	Down	Up	Down	Up	Down	Up	Down	Up	Down
Mn	0.90	1.20	0.92	1.20	0.95	1.20	0.98	1.20	0.99	1.20
Cu	0.51	1.50	0.62	1.55	0.70	1.70	0.80	1.90	0.89	2.05
Mg	0.50	1.55	0.61	1.60	0.69	1.75	0.79	1.95	0.89	2.10
Zn	0.45	1.60	0.55	1.70	0.63	1.90	0.75	2.10	0.87	2.40
Fe	0.20	1.80	0.35	2.00	0.49	2.30	0.61	2.60	0.80	2.80
Si	0.10	2.00	0.22	2.50	0.39	2.50	0.55	3.00	0.75	3.40

Figure 49 shows the normalized cost savings of each of these scraps compared to the base case for various stages in the refining process. All four cases have higher possible cost savings than the 5XXX series base case. The UBC, 5184, and 6061 extrusion scraps all reach their maximum possible cost savings even earlier in the refining process; at approximately 83% upgrade yield compared to 75% upgrade yield for the base case. The possible cost savings for the 5184 and 6061 extrusion scrap follow a similar trend, reaching a maximum savings of approximately 1%. The UBC scrap savings seem to plateau off with increased refining beyond 70%. As shown in Figure 49, the casting scrap has dramatically higher possible cost savings, modeled as high as 70%. This is most likely due to the high level of silicon in casting scraps and the favorable compositional multipliers for silicon associated with the fractional crystallization process (cf. Table XXVI). It is important to note, however, that the multipliers calculated here may be less accurate for scraps that differ dramatically in composition to the base case 5XXX series scrap due to differing intermetallic reactions with increased impurity levels. An intermetallic is a compound of two metals that has a distinct chemical formula; these are an intermediate phase that exists over a very narrow range of compositions in the phase diagram. Looking at the copper-aluminum system (cf. Figure 43), one can see an example of an intermetallic ($CuAl_2$) that forms around 33 at.%. This means that the cost savings, with the exception of the base case and alloy scrap 5184, may be more uncertain.

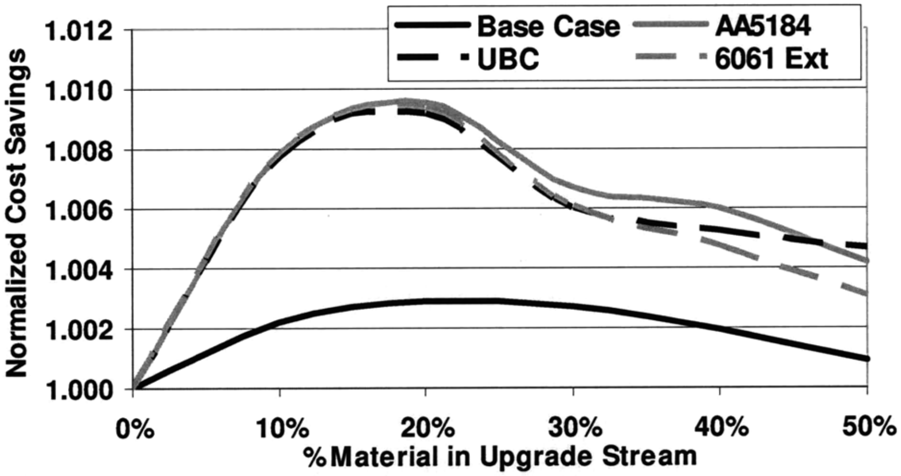


Figure 49. Normalized cost savings for the original 5XXX scrap from the Alcoa study as well as three other types of common wrought scraps

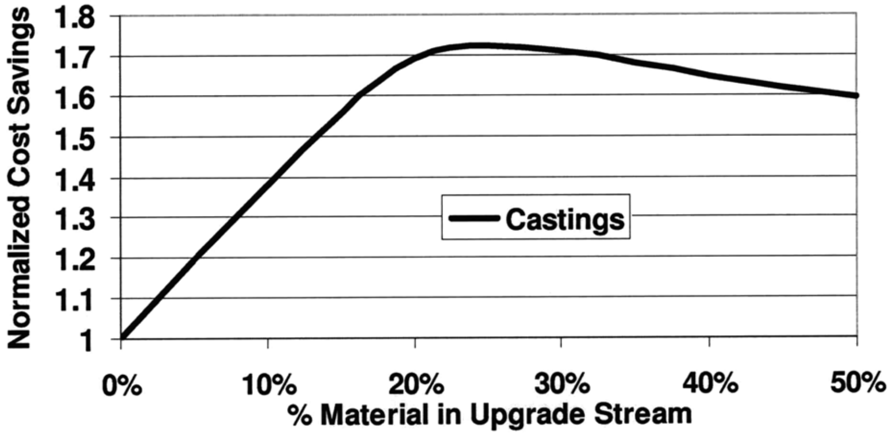


Figure 50. Normalized cost savings for cast scrap for various stages of the refining process

5.2.5 Discussion

Demonstrated on a fractional crystallization refining technology, the framework was used to identify maximum cost savings for a base case scrap as well as extended to four other types of scraps materials with differing initial compositions. Results suggest that the technology achieves maximum benefit after only limited refining, at approximately 20% upgrade yield, and the value is strongly dependent on the specifics of the raw material to be upgraded. Examining how equilibrium distribution coefficients are calculated highlights the necessity of sensitivity analysis surrounding resulting composition. These coefficients indicate that scrap streams high in silicon and iron would see the most benefit from this type of upgrading technology; results shown in this section would support this conclusion. This indicates much promise for fractional crystallization as an upgrading technology as both silicon and iron are cited as being two of the most problematic in aluminum scrap streams (cf. chapters 1 and 2).

5.3 Conclusions

To address the problem of impurity element accumulation in secondary materials, many upgrading technologies exist both in industry and at the research and development stage. The use of linear programming batch plans presented here provides a preliminary tool to assess the possible environmental and economic impact of these technologies to secondary production decision-making. The framework shown here can be applied to a variety of other upgrading technologies with little to no modification. As stated in previous chapters, an important addition to this analysis will be the extension of the single period batch mixing model to a multiple generation mixing model capable of characterizing a closed or open loop recycling system. This extension will first require a characterization of the flows of end-of-life scrap materials over time.

Chapter 6. Modeling the flow of end-of-life aluminum scraps

To quantify the value of an upgrading technology over time requires two key pieces of information as outlined in previous chapters, 1) the time-dependent flows of scrap materials must be characterized, and 2) these must be combined with the linear programming batch planning that was used in Chapter 5. This addition is necessary to understand the opportunities afforded by optimal allocation of scrap materials as well as the economic implications of using any upgrading technology.

It is hypothesized that the time-independent value of upgrading will equal the time-dependent value if the behavior of the recycling system is static, i.e. there are no transient or dynamic behaviors present. However, as outlined in Chapter 2, it is well known that material systems are quite dynamic. In particular, as highlighted in Chapter 1, the availability of both prompt and end-of-life scraps as well as their compositions are two such dynamic elements; these factors have a large impact on batch planning decisions for time-independent analysis. This chapter explores the impact of these dynamic elements, such as composition and availability, on the value of upgrading using time-dependent analysis.

6.1 Scrap availability

6.1.1 Demand or production

As outlined in Figure 15, aluminum is used by the following major industrial sectors: containers and packaging, transportation, construction, electrical, consumer durables, and machinery and equipment. The specific products and alloys included in these aggregate categories will be discussed in 6.2. Figure 51 shows the production of each of these categories in the United States from 1975-2003. Overall, production has been increasing in the US over this time frame with the largest gains being in the transportation category. This is due to the introduction of more aluminum in the car (for example, in castings, transmissions, and radiators) for light-weighting purposes in recent years (Schultz 2008). For Figure 51, all other products not classified in these sectors are tracked as "other" and exports are reported as well.

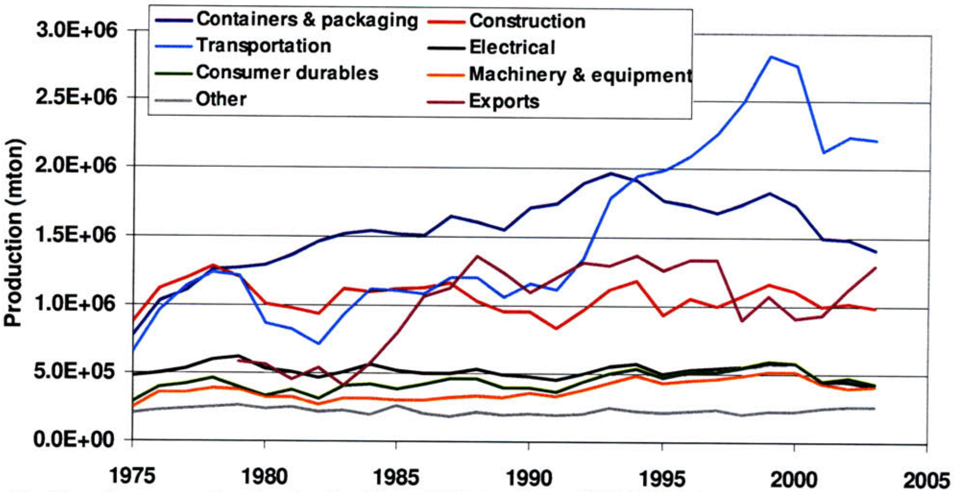


Figure 51. Aluminum production in the United States from 1975-2003 broken into major product categories(Kelly and Matos 2006)

To forecast future demand or production, the trends for these aggregate categories were examined in more detail. A combination of regression analysis and industry knowledge was used to generate forecasts; the general behavior and forecast equations are summarized in Table XXVII. One can see that several production numbers are forecasted to plateau (containers, construction, and other) while some are increasing (transportation and consumer durables) or decreasing (electrical). These forecasts reflect current trends, for example, the use of lightweight materials in the automobile is expected to increase (Gorban, Ng et al. 1994; Gesing 2004). The recent economic downturn has been neglected because the most recent production numbers are not available yet and the assumption that the longer term trends will dominate future behavior. The resulting forecasts are shown in Figure 52 along with the previous actual production numbers.

Table XXVII. General trend behavior and forecast equation for each of the aggregate product categories

Category	Behavior	Forecast value or equation
Containers and packaging	Plateau	175000
Construction	Plateau	100000
Transportation	Increasing	542631*ln(x) + 173819
Electrical	Decreasing	-1036.9*(x) + 532416
Consumer durables	Increasing	6100*(x) + 352879
Machinery and equipment	Increasing	6339*(x) + 283323
Other	Plateau	250000
Exports	Increasing	278009*ln(x) + 358660

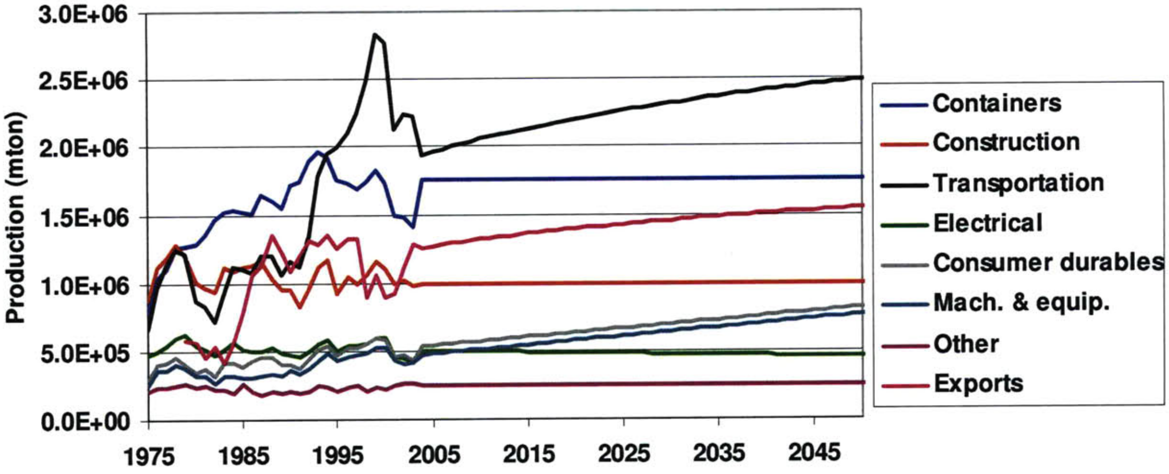


Figure 52. Aluminum production in the United States from 1975-2003 broken into major product categories(Kelly and Matos 2006) plus forecasted production for 2004-2050

6.1.2 Lifetime

To project the amount of scrap reaching end-of-life, a residence time model was used, as discussed in Chapter 2. For this model, a mean lifetime and standard deviation on that lifetime are assumed; these are listed in Table XXVIII for the major aluminum product categories.

Because most containers and packaging reaching end-of-life are used beverage cans, the lifetime on these products is quite low; the time from production to consumption of the beverage to the beverage can reaching a scrap yard can be as low as six months. Construction scrap reaching end-of-life typically is due to either renovation or demolition. For demolition, the aluminum would have a similar lifetime to a building (i.e. typically greater than 50 years) while for renovation, the lifetime would be closer to 15 years, resulting in a large standard deviation(Jolly 2005). Electrical scrap is mainly from building wiring and therefore will reach end-of-life by the same mechanisms as construction and building scrap (i.e. renovation and demolition). However, wiring is more likely to be replaced in renovations and therefore has a slightly shorter lifetime; this lifetime was assumed to be similar to that of copper wiring(Jolly 2005). Transportation scrap has an average lifetime of an automobile (Davis, Diegel et al. 2008); boats, trucks, and aircraft are assumed to have similar lifetimes. Consumer durables, as well as machinery and equipment have the largest uncertainty in lifetime due to the wide range of products included in these categories. These were estimated from work done by (Bruggink 2000).

Table XXVIII. Aluminum product categories, their average lifetime in years, and the standard deviation of that lifetime

	Lifetime	Std. Dev.
Containers & Packaging	1	2
Building & Construction	35	15
Transportation	15	5
Electrical	20	10
Consumer durables	4	2
Machinery and equipment	10	3
Other	2	1

The resulting percentage reaching end-of-life at some year from production is shown in Figure 53. A normal distribution was assumed for these lifetimes; many others including lognormal, weibull, and gamma have been used in other work (Bruggink 2000; Hatayama, Yamada et al. 2007). On the extremes of the spectrum are containers and packaging on one end and construction scraps on the other. Nearly all of the container scrap reaches end-of-life within three years after production. One can see that even fifty years from production, not all building and construction scraps have reached end-of-life.

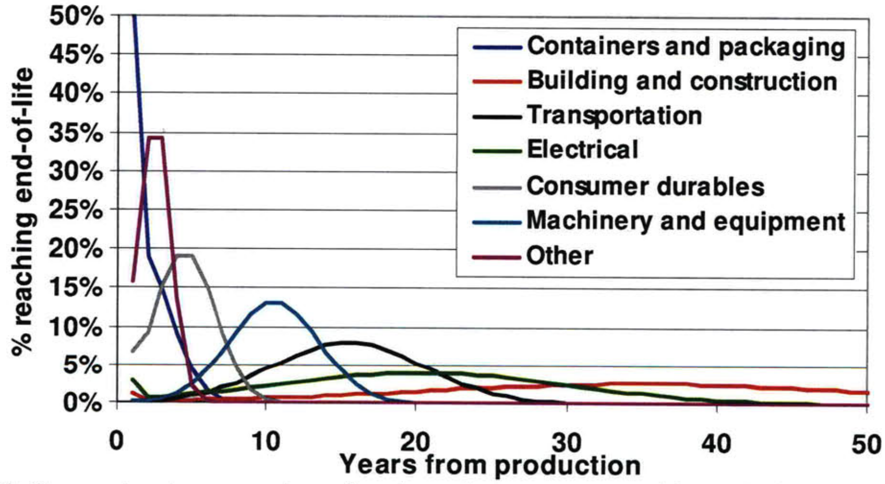


Figure 53. Curves showing percentage of each product category reaching end-of-life in years since production

6.1.3 Collection

The amount of a scrap reaching end-of-life at any given year will equal the total possible availability for that year. However, because there is not 100% collection for any of these product categories, actual availability will always be less than this. Collection rates for product categories vary as much as their production volumes and lifetime; few are accurately tracked. The one product that has a well characterized collection rate is used beverage cans, the largest component in the containers and packaging category. Data from the Container Recycling Institute is shown in Figure 54 for used beverage can recycling rates from 1986 to 2006[14].

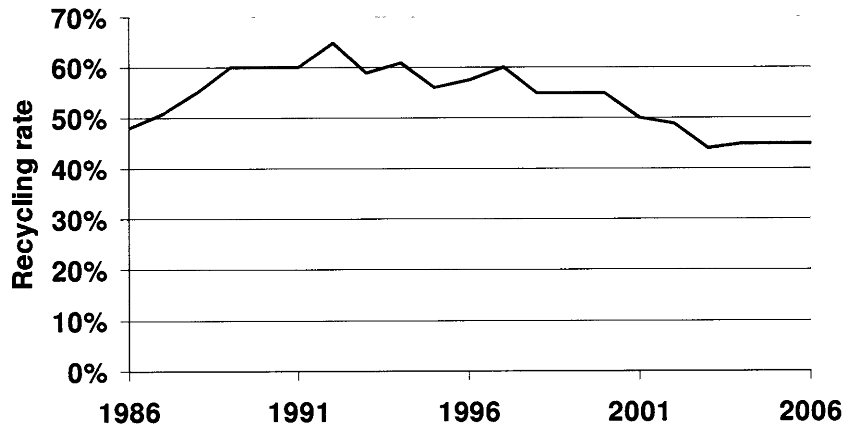


Figure 54. Recycling rate for used beverage cans in the US from 1986-2006(Institute 2007)

Although the USGS tracks both total production and amount of scrap utilized each year for the United States, it is not possible to calculate collection rates due to the added complications of product lifetimes, exports, and dissipative uses. However, it is useful to examine this data to inform current recycling rate trends. Figure 55 shows that while total scrap collected is going up, the portion made up by each category has been changing over recent years. In particular, the percentage of scrap use in the US has been shifting from UBC's and castings to more shredded aluminum from automobiles and other categories.

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[14] The Container Recycling Institute provides an example on how they calculate the used beverage can recycling rate for the US using 2004 numbers. All numbers in billions of cans. Recycling rate = cans recycled that were originally sold in the US/domestic cans available for recycling. The number of cans recycled that were sold in the US (the numerator)= the number of collected cans recycled domestically and exported (51.5) – the number of imported scrap cans (6.3) = 45.2. Number of cans available for recycling in the US (the denominator)= new cans made and shipped in the US (100.5) + new imported unfilled cans (0.7) - new exported unfilled cans (1.1) = 100.1. Therefore, recycling rate for 2004 = 45.2/100.1 = 45.1%

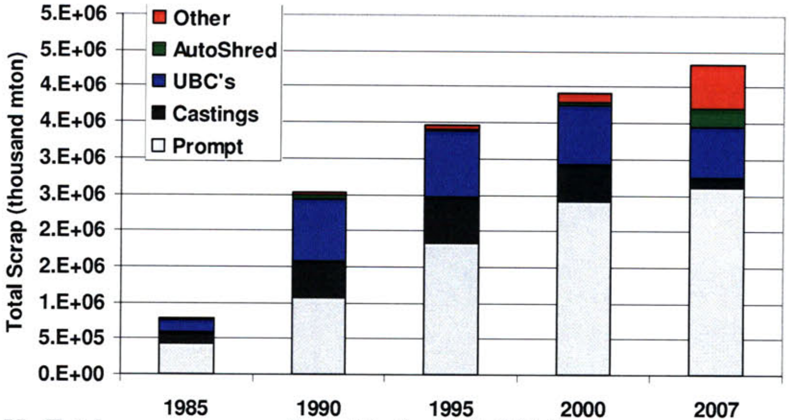

Figure 55. Total amount scrap collected in the United States for several year snapshots

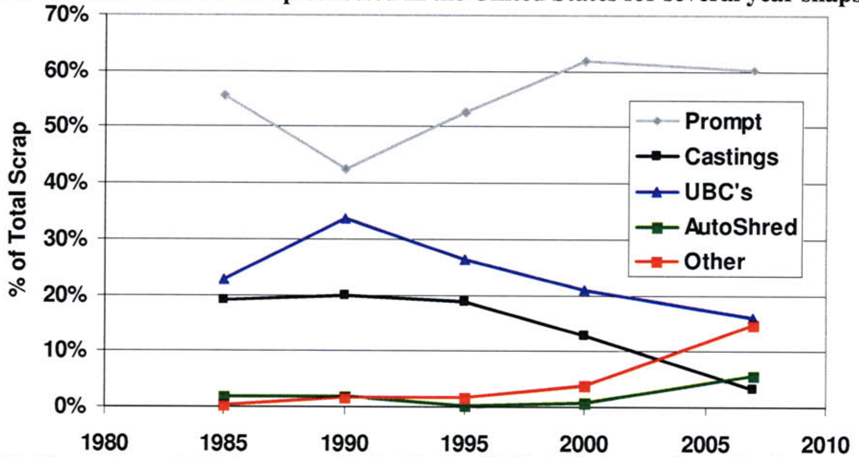

Figure 56. Percentage of total scrap collected in the United States made up by the top recycled categories for several year snapshots (1985, 1990, 1995, 2000, and 2007)(Kelly and Matos 2006)

These shifts in utilization and recycling rates combined with the inaccessibility of most scrap collection data make assumptions surrounding collection quite uncertain. For results presented in this chapter, the collection rate was assumed to be the same over the multiple years examined. However, this methodology allows for collection rate to be a dynamic element of the end-of-life flows analysis. Collection rates were found in the literature for several categories; these are listed in Table XXIX along with the reference. For collection rates that could not be found in the literature, an estimate using collection from two studies(Bruggink 2000; Hatayama, Yamada et al. 2007) presented in Chapter 2 were used.

Table XXIX. Aluminum product category and estimated collection rates from two previous studies as well as assumed values for this thesis

	(Bruggink 2000)	(Hatayama, Yamada et al. 2007)	This study	Ref
Containers & Packaging	25-60%	-	50%	(Institute 2007)
Building & Construction	15%	80%	55%	(Rodriquez 2007)
Transportation	80%	90%	85%	
Electrical	10%	30%	25%	(Jolly 2005)
Consumer durables	20%	40%	30%	
Machinery and equipment	15%	10%	12.5%	
Other	-	20%	20%	

6.1.4 Availability summary

Actual and forecasted production numbers determine the amount of a certain product category being manufactured in a given year. This is fed into the residence time model which will calculate the percentage reaching end-of-life for a given year in the future. The amount actually available will be modified by the assumed collection percentage for that category. The resulting projected availability is shown in Figure 57. Production starts at 1975 in this model; it takes several years after 1975 to show an accurate picture of what the returning scrap stream includes because longer lifetime scraps will not become available for several years. For example, because containers have such a short lifetime, they make up an unrealistic portion of the scrap stream before 1990 (Figure 58). One can see there is a shift from containers to transportation being the largest portion of available scrap in the future; this shift may be occurring already (cf. Figure 56).

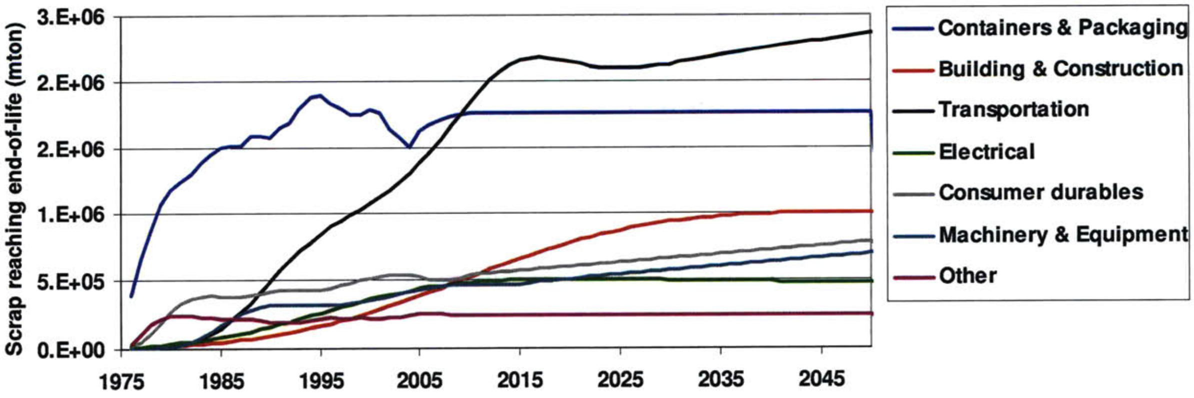

Figure 57. Modeled/projected aluminum scrap availability in the US

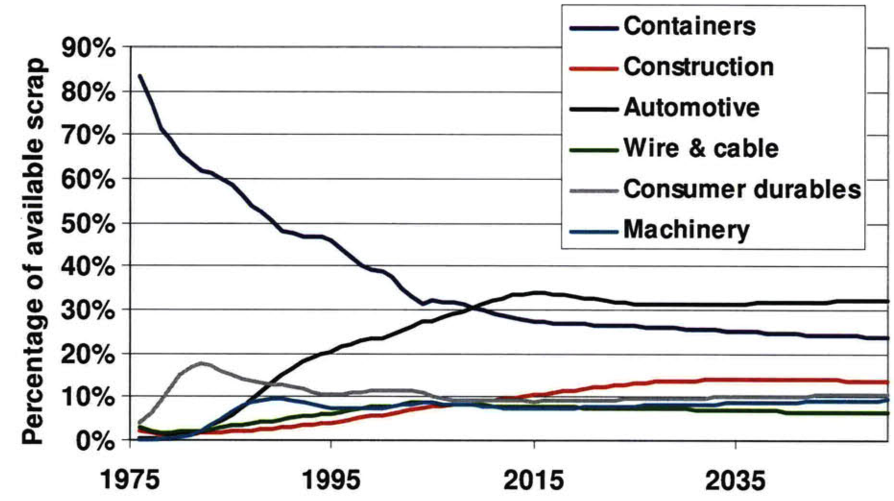

Figure 58. Percentage of available scrap belonging to each product category

6.2 Scrap composition

The composition of returning scrap materials is another dynamic element of material recycling systems that can have a large effect on batch planning decisions. While the above parameters help to define an overall amount of scrap returning, details of which alloys are included in the aggregate categories are required to track composition. Compositional details are frequently not captured in end-of-life material flow models as detailed in Chapter 2. The alloys produced can be quite uncertain because the breakdown of alloys within the larger product categories are not tracked by the USGS or IAI. Motivation for the selection of the case used in this work is summarized in the next section.

6.2.1 Selection of alloy case

The large number of complexities already present in the aluminum recycling system motivates selecting a representative set of alloys for tracking composition as opposed to attempting to capture all of the alloys currently produced. For example, the Aluminum Association reports specifications for over 500 registered alloys[15] and this does not include custom alloys often developed within aluminum companies. The alloy breakdown in products selected for this case was chosen to best capture the alloys that make up the majority of returned scrap according to USGS (cf. Figure 12).

Specifically, used beverage cans, shredded automotive scrap and castings, and mixed wrought scraps make up the majority of end-of-life scrap collected in the US. For this

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[15] Number of registered Aluminum Association alloys by series family: 1XXX = 40, 2XXX = 74, 3XXX=39, 4XXX=29, 5XXX=94, 6XXX=85, 7XXX=71, 8XXX=35, and cast=41

case, the products included in the containers and packaging category are those in UBCs, 3004 and 3104 can body and 5005 aluminum alloy for the tab. Construction scrap consists mainly of siding, window frames, and corrugated roofing which includes, 3105, 6063, and 3004 wrought sheet, respectively. An appropriate selection for transportation is more complicated. Alloys included in transportation scrap encompass a wide range of alloys; typical applications and their alloys are outlined in Table XXX.

Table XXX. Major automotive applications and alloys (reproduced from(Gesing 2004))

Application	Alloy
Engine Castings	B319, 356, 381
Wheels	A356.2, 5754
Radiators	1100, 3003
Structural Sheet	2036, 5182
Extrusion	6061, 6063, 6082
Closure Sheet	6016, 6022, 6111
Bumpers	7003, 7129

For this case, one engine casting (380), 7003 alloy for bumpers, and the most common body sheet used in doors, hoods, and trunks (6061) were selected. For electrical applications, the most common product is household wiring which consists of Stabiloy©, an 8030 alloy. Other electrical applications typically use 1350 alloy. The selection of alloys for the consumer durables and machinery and equipment categories is also not straight forward. There are a wide variety of applications that fall within these categories including: zippers (5056), fins (1100), furniture (6063), screens (5056), appliance trim (5252), welded structures (5454), rivets (2024), builder's hardware (5050), storage and pressure vessels (5454), pipe railing (6063), hydraulic tubing (5052), TV towers (5086), and propellers (2025). Again, the representative alloys chosen attempt to capture which products are the most likely to be recycled. For consumer durables, appliances (5005) and utensils (6111) were chosen while for machinery and equipment, storage tanks (5052) and lithography sheet (1100) were selected. For the "other" category, one common product is aluminum for steel deoxidization. This is an important material flow to capture as it is dissipative. A common aluminum product that also does not fit into any of the aggregate categories is 2036 alloy for pistons. These selections are summarized in Table XXXI; their maximum and minimum AA specifications are listed in Table XXXII and Table XXXIII.

Table XXXI. Selected representative alloys for case and the main form of returning scrap

Category	Alloy	Returning scrap
Containers and packaging	3004 can body	Used beverage can
	3104 can body	
	5005 tab	
Building and construction	3105 siding	Co-mingled sheet and bar
	6063 window frames	
	3004 corrugated roofing	
Transportation	380 auto castings	Auto shred
	7003 bumpers	
	6061 body sheet	
Electrical	8030 Stabiloy© wire	Wires
	1350 conductors	
Consumer durables	5005 appliances	Mixed scrap
	6111 utensils	
Machinery and equipment	5052 storage tanks	
	1100 litho sheet	
Other	Steel deox	Does not return
	2036 pistons	Mixed scrap

Table XXXII. Maximum AA specifications for products included in the case study

	Si	Mg	Fe	Cu	Mn	Zn
3004 can body	0.0030	0.0130	0.0070	0.0025	0.0150	0.0025
3104 can body	0.006	0.013	0.008	0.0025	0.014	0.0025
5005 tab	0.003	0.011	0.007	0.002	0.002	0.0025
3105 siding	0.006	0.008	0.007	0.003	0.008	0.004
6063 window frames	0.0060	0.0090	0.0035	0.0010	0.0010	0.0010
3004 corrugated roofing	0.0030	0.0130	0.0070	0.0025	0.0150	0.0025
380 auto castings	0.095	0.001	0.02	0.04	0.005	0.03
7003 bumpers	0.003	0.01	0.0035	0.002	0.003	0.065
6061 body sheet	0.0080	0.0120	0.0070	0.0040	0.0015	0.0025
8030 Stabiloy© wire	0.001	0.005	0.008	0.003	0	0.005
1350 conductors	0.001	0	0.004	0.0005	0.0001	0.0005
5005 appliances	0.003	0.011	0.007	0.002	0.002	0.0025
6111 utensils	0.0110	0.0100	0.0040	0.0090	0.0045	0.0015
5052 storage tanks	0.0025	0.0280	0.0040	0.0010	0.0010	0.0010
1100 litho sheet	0.0095	0	0.0095	0.002	0.005	0.001
Steel deox	0.2	0.2	0.2	0.2	0.2	0.2
2036 pistons	0.005	0.006	0.005	0.03	0.004	0.0025

Table XXXIII. Minimum AA specifications for products included in the case study

	Si	Mg	Fe	Cu	Mn	Zn
3004 can body	0.0000	0.0080	0.0000	0.0000	0.0100	0.0000
3104 can body	0	0.008	0	0.0005	0.008	0
5005 tab	0	0.005	0	0	0	0
3105 siding	0	0.002	0	0	0.003	0
6063 window frames	0.0020	0.0045	0.0000	0.0000	0.0000	0.0000
3004 corrugated roofing	0.0000	0.0080	0.0000	0.0000	0.0100	0.0000
380 auto castings	0.075	0	0	0.03	0	0
7003 bumpers	0	0.005	0	0	0	0.05
6061 body sheet	0.0040	0.0080	0.0000	0.0015	0.0000	0.0000
8030 Stabiloy© wire	0	0	0.003	0.0015	0	0
1350 conductors	0	0	0	0	0	0
5005 appliances	0	0.005	0	0	0	0
6111 utensils	0.0060	0.0050	0.0000	0.0050	0.0010	0.0000
5052 storage tanks	0.0000	0.0220	0.0000	0.0000	0.0000	0.0000
1100 litho sheet	0	0	0	0.0005	0	0
Steel deox	0.2	0.2	0.2	0.2	0.2	0.2
2036 pistons	0.005	0.006	0.005	0.03	0.004	0.0025

6.2.2 Composition summary

The composition of scrap materials will be the co-mingled, weighted average of the alloys that were used to manufacture them. Six elements were tracked for each of the seventeen material streams; this generates a large amount of compositional data. To see the overall trend of compositional drift resulting from the above production, lifetime, collection, and alloy assumptions, the compositional data was aggregated to one number shown for each element in Figure 59. One can see that overall, silicon, copper, and zinc are increasing in the scrap stream with silicon being the most significant. The weight fraction of these elements is quite small due to the extreme amount of dilution with primary that is occurring. This is because the available amount of scrap is much smaller than production in each year. Magnesium and manganese are decreasing while iron stays fairly constant through-out the modeled time period. The drift in composition is directly linked to the availability of scraps; for example, transportation production is increasing over this time period and castings are a significant portion of recycled automobiles. These castings are quite high in silicon which therefore may have pushed the silicon composition of the aggregate scrap stream higher. The peak is due to the peak in transportation production around 1995 (cf. Figure 52). UBCs will have a relatively significant amount of magnesium and manganese when compared to some of the other scrap types. Because their production levels out over this time frame, this may drive the decrease and flattening out of aggregate magnesium and manganese within the system.

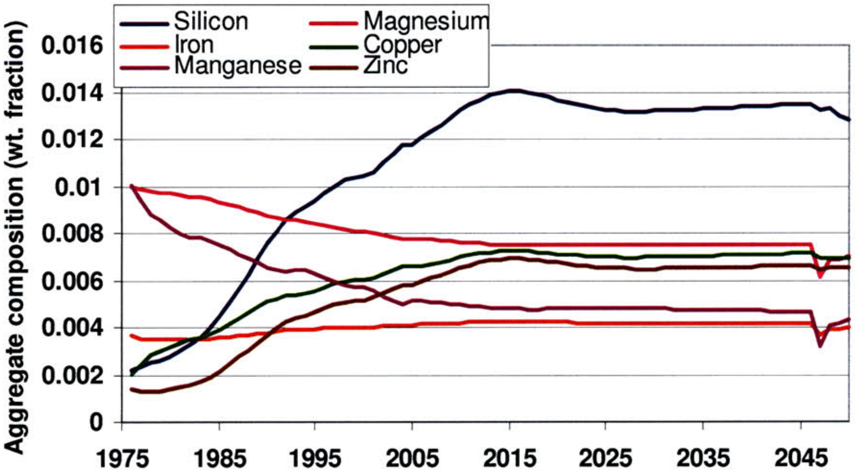


Figure 59. Composition over time for the aggregate scrap stream

6.3 Batch planning within dynamic material flows

Chapter 2 outlined much of the literature that has modeled dynamic material flows and examined accumulation issues. It was found that one of the key pieces missing from this work was the blending decisions made by secondary producers. Specifically, what mix of scraps, primary, and alloying elements the producer will allocate to the alloys being manufactured. This is a key element to capture because operational strategies can be just as important as technological strategies in mitigating accumulation (cf. section 1.3.1). This becomes very clear if one were to use the dynamic materials flow analysis methodology described above to examine how scrap compositions change over time with and without optimal allocation of scrap materials occurring. Without batch planning, the resulting compositions are based solely on the combination of the statistics presented above, i.e. production, lifetime, collection, and average composition. With the addition of batch planning to this methodology, the producer can allocate the available scrap materials optimally. When the composition of certain scraps becomes problematic for their use in a certain scrap stream (usually this is because they are too high), optimal allocation allows the producer to put those scraps into different alloy products. This enables better control of elements within the scrap stream which can significantly lower tramp element composition as shown by the modeled results in Figure 60-Figure 62. The dotted lines show how the aggregated composition would change over time according to statistics while the solid lines show the same compositions but with optimal allocation ie. the addition of blending models to the dynamic material flow analysis.

For all elements, the compositions are the same initially, as they have had the same parameters from the year 1975 to 2000. Figure 60 shows that for silicon and copper, while initially higher with optimal allocation, over time, their accumulation is significantly less, for silicon 20% less and for copper 25% after fifty years of modeled behavior (1975-2025). Optimal allocation also significantly mitigates accumulation of magnesium and manganese within the aggregate scrap stream as well (Figure 61). The composition of magnesium is 24% less with allocation compared to the statistical value and 47% less for manganese. Figure 62 shows that for zinc, the optimal allocation actually results in a slightly (7%) higher composition, although it tracks quite closely to the statistical value. However, for iron the difference is quite dramatic, optimal allocation shift the composition of the scrap stream 69% less when compared to the statistical value. This suggests that optimal allocation is a strategy that can be quite effective at mitigating accumulation over time.

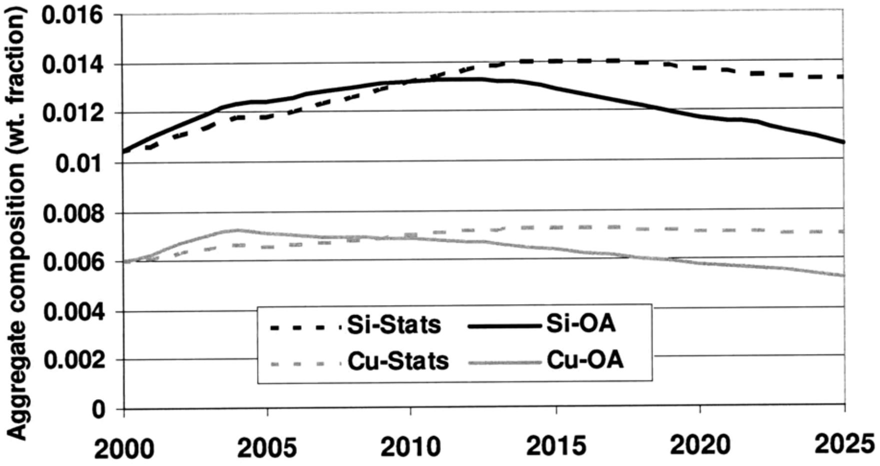


Figure 60. Aggregate silicon and copper composition for dynamic material flow analysis without optimal allocation based solely on statistics (Stats) and with optimal allocation (OA) of scraps

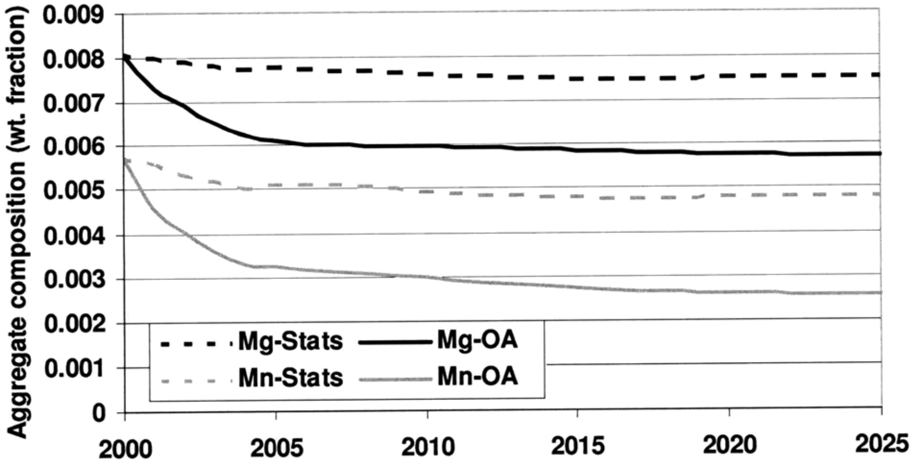


Figure 61. Aggregate magnesium and manganese composition for dynamic material flow analysis without optimal allocation based solely on statistics (Stats) and with optimal allocation (OA) of scraps

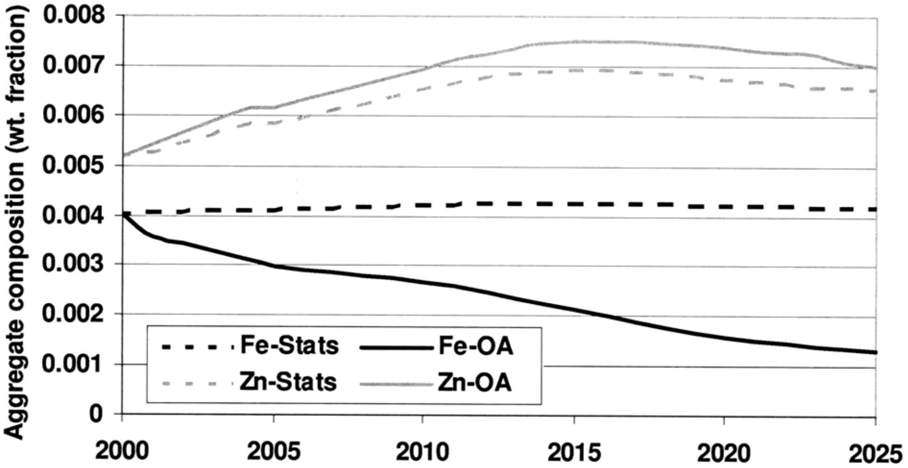


Figure 62 Aggregate iron and zinc composition for dynamic material flow analysis without optimal allocation based solely on statistics (Stats) and with optimal allocation (OA) of scraps

With this combination of dynamic material flow analysis for the US aluminum recycling system and blending models, a methodology has been developed that has the capability of evaluating the time-dependent value of upgrading technologies. This combination has also already served to answer part of one of the thesis questions: 1) How effective are operational or technological strategies at mitigating accumulation? Figure 60 showed that operational strategies, specifically, optimal allocation of available scrap materials, can have a profound effect on lowering overall accumulation. The next chapter will focus on the technological strategies and address the second question: under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams? Two specific cases within the overall recycling system will be re-visited to answer this question, the same technologies analyzed in Chapter 5: sorting and dismantling of aerospace scraps and fractional crystallization of co-mingled scraps.

Chapter 7. Time-dependent evaluation of upgrading technologies

This chapter will answer the following questions using the methodology developed in the previous chapters:

1) How effective are operational or technological strategies at mitigating accumulation?
2) Under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams?

In order to examine the time-dependent value of upgrading technologies in the context of the aluminum recycling system, the two cases considered in chapter 5 will be examined again, a refining technology, fractional crystallization, and physical upgrading technologies, sorting and dismantling. The first case describes the addition of time dependence to the case of sorting and dismantling aerospace scraps.

7.1 Time-dependent behavior regimes

Does the value of upgrading change when considering time? This work hypothesizes that a time-independent snapshot of an upgrading technology value will not change when considering multiple generations if the recycling system is in equilibrium. It is therefore imperative to identify the key parameters that would cause a recycling system to be dynamic or changing over time. Two key dynamic aspects of the scrap stream that can have significant influence on blending decisions as outlined in previous chapters are: availability and composition. Factors influencing scrap availability are production, collection, and product lifetimes. Increasing production or demand means that there is comparably less scrap material available. Increasing collection rates will increase the scrap availability. Longer product lifetimes can constrain availability by shifting forward the time in which the end-of-life materials will be collected. The composition of the scrap stream can change due to differing batch plans from generation to generation as well as the mixing of materials to create products. More significant compositional drift will occur when there is additional pick-up or contamination from end-of-life processing or co-mingling or differing products and scrap types (composition increasing).

These four regimes of changing availability and composition are outlined in Figure 63. The behavior of the recycling system in these regimes will be discussed from the least constrained to the most constrained as numbered below. All four regimes are present in the sorting and dismantling of aerospace scraps case while increasing availability is related closely to the degree of refining for the fractional crystallization case. This will be explained in more detail in section 7.3

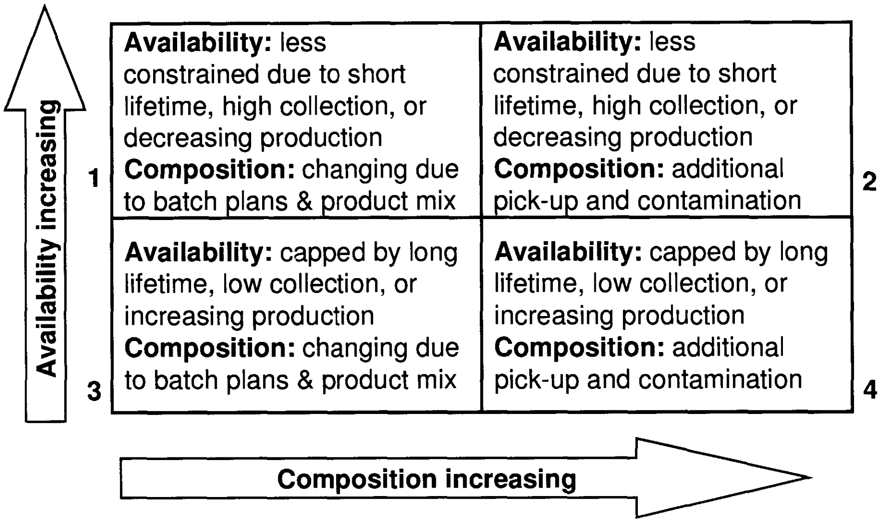


Figure 63. Four main regimes of changing composition and availability that will be explored for the dismantling and sorting aerospace scrap case.

For the subsequent time-dependent analysis, a discount rate of zero was assumed for the costs. There are many methods for determining an appropriate discount rate to use for analyzing costs over time; a capital asset pricing model is a relevant one for this type of work (White, Case et al. 2009). In this method, one would examine the price of the material of interest over several years and determine its volatility relative to the overall market. In the case of most metals, and certainly in the case of aluminum and bauxite, the inflation adjusted price has actually been going down over the last century (Figure 64A & B). This would indicate a negative rate of return for the given volatility (σ) of aluminum prices over this time frame. For capital asset pricing models, this rate of return is compared to a risk-free investment in order to extrapolate a discount rate, typically a US treasury note is used. Currently, the return on US T-notes is quite low, 0.14% for a one month and 0.53% for a one year. This timeframe for T-notes matches to the time-period where decisions are being made from the perspective of the secondary producer, i.e. less than one year. Therefore, a discount rate of zero was determined to be appropriate for the analysis included in this thesis according to the following equation:

$$\text{rate of return} = \text{Tbill} + \beta\sigma \tag{7.1}$$

where β is the slope of rate of return plotted against volatility. However, there have been periods of time when investing in metals had a higher rate of return. In these cases, a discount rate higher than zero may be appropriate for time dependent analysis. If one were to optimize over the entire system, taking a different stakeholder perspective as described above, then including a discount rate analysis would push the decision-maker towards short term solutions. This may have a large impact on the selection of upgrading technologies as well as optimal allocation of scrap materials. This impact is examined with the sensitivity analysis in section 7.2.4.

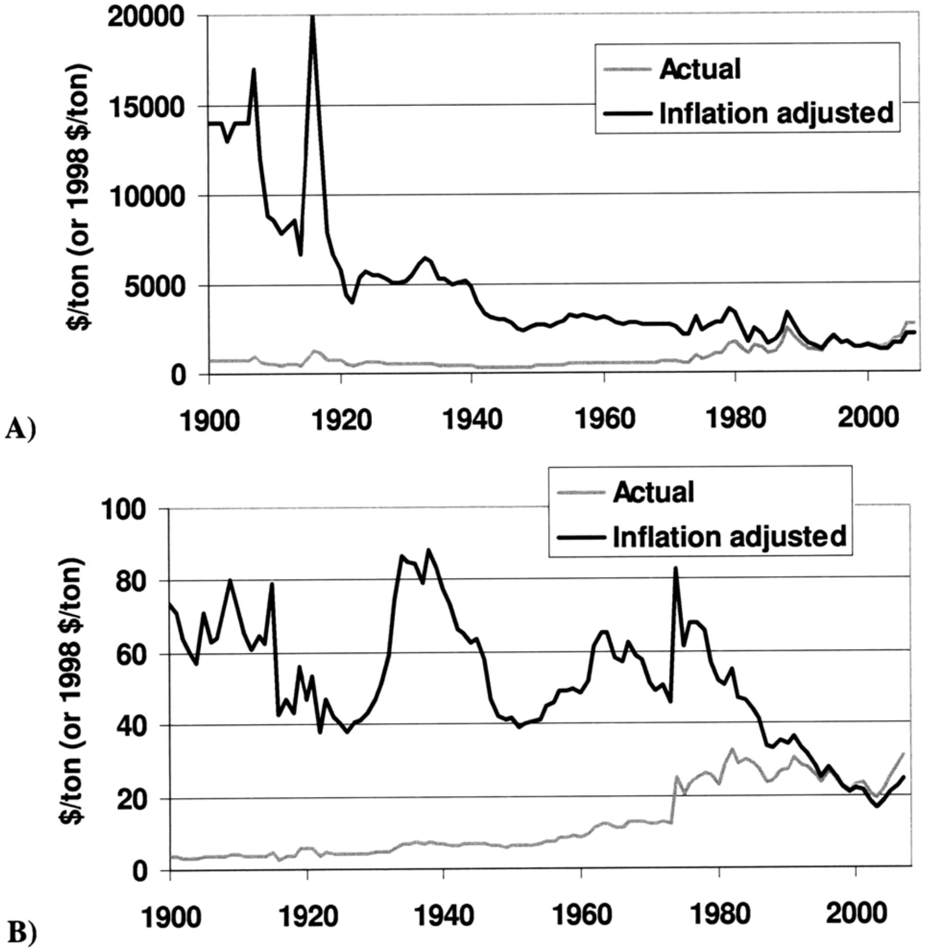


Figure 64. A) Aluminum and B) bauxite prices in the US over the last century, both actual and inflation adjusted by 1998 prices(Kelly and Matos 2006)

7.2 Sorting and dismantling aerospace scraps

7.2.1 Review of time-independent value of sorting and dismantling

To keep the computational complexity of the multi-generation model low as outlined in section 3.4, the mean based linear programming batch planning model was used for this analysis. Also, the dismantled case, described in chapter 5, was simplified to include only four major aerospace alloys: 2014, 2024, 7074, 7178. These were selected because they were also included in the production portfolio. Considering multiple generations requires some matching between the scrap and production portfolio in order for the composition of the products to become the composition of the scraps in future generations. This more simplified case study combined with the mean-based method will result in slightly altered numbers from the base case presented in Chapter 5 and therefore the values for each of the three end-of-life options are shown in Table XXXIV. All other parameters (scrap composition, product specifications, and price) are the same as the case presented in Chapter 5 (Table XIX).

Figure 65 shows the scrap utilization (percentage of scrap in the production portfolio) for the alloys produced. Besides the four aerospace alloys, utilization is generally quite low for all three end-of-life options: dismantled, sorted, and co-mingled. The aerospace alloys, on the other hand, are able to use nearly all scrap for their production for the sorted and dismantled cases. The value of sorting or dismantling the co-mingled scrap stream could be interpreted as the difference in production cost between those cases. This time-independent batch plan would indicate a value of sorting of \$434 (\$0.29/lb.) and value of dismantling of \$513 (\$0.34/lb.).

Table XXXIV. Total production cost and scrap usage for the co-mingled, sorted, and dismantled cases

	Co-mingled Case	Sorted	Dismantled
Total Cost	\$3,196	\$2,757	\$2,683
Cost/lb.	\$2.13	\$1.84	\$1.79
Scrap usage	252.6	568.6	621.9

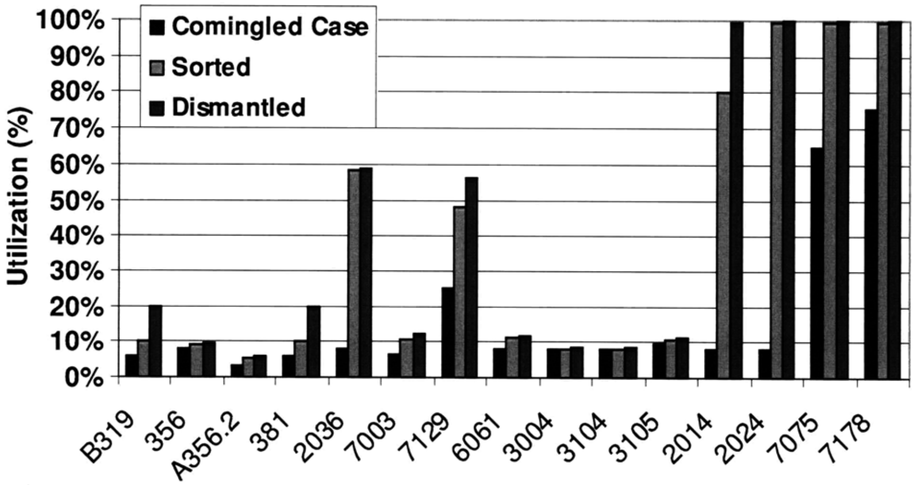


Figure 65. Scrap utilization (percentage of portfolio made up of scrap) by product for all three cases

7.2.2 Time-dependent value of sorting and dismantling

Regime 1 (cf. Figure 63) is considered the closest to equilibrium or static behavior in terms of dynamic elements within the recycling system. This regime occurs when composition is changing due to varying batch plans and product mixing without additional contamination or pick-up occurring. Therefore compositional drift is less significant. In terms of availability, lifetimes, collection and production are such that available scrap is greater than the amount that can be used due to compositional limitations. Figure 66 shows fairly consistent production costs over the tracked time period which would indicate the system is fairly close to equilibrium state as hypothesized.

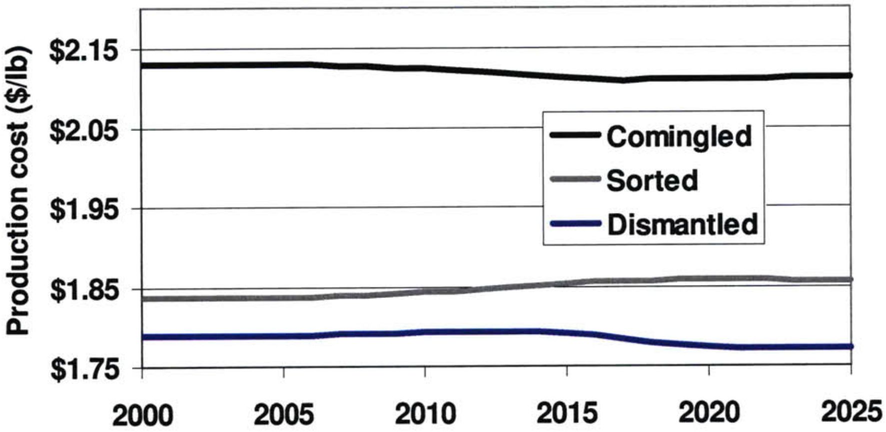


Figure 66. Time-dependent production cost for the three cases in Regime 1 (low compositional drift, less constrained availability)

In aggregate, the production cost typically tracks with scrap usage as the scrap materials are less expensive than primary aluminum and most alloying elements. Figure 67 shows this to be the case; for example, scrap usage for the co-mingled case increases slightly over time which is why the production cost decreases slightly over this time frame. One can see that for this regime of low compositional drift and less constrained availability, most alloys produced have generally static scrap utilizations, hence the fairly static production cost curves. However, this is only the aggregate behavior; each of the individual alloys produced may have slightly changing utilization over this time period depending on how the available scraps are allocated as shown in Figure 68. For example, as the scrap utilization for alloys 7003 and 6061 begins to slump over time (they cannot use as much scrap in their production due to compositional constraints), that available scrap is pushed into other alloys such as 356, 7178, and B319 whose utilization begins to pick up. This is how optimal allocation can control compositional drift and keep production costs steady over this time period.

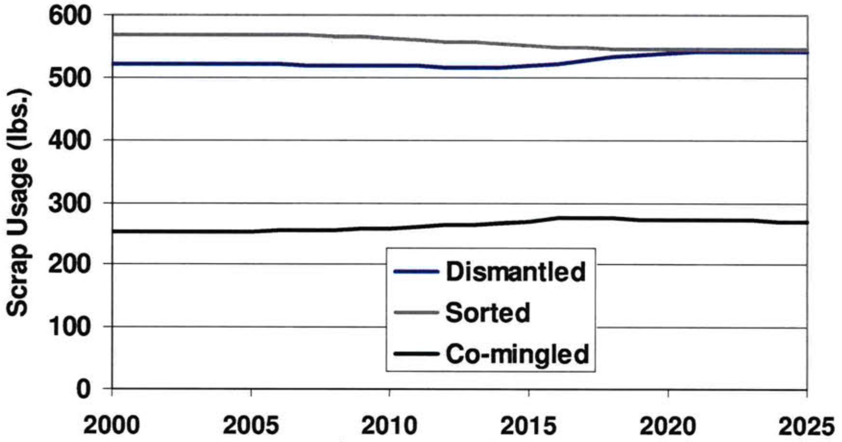


Figure 67. Time-dependent scrap utilization for the three cases in Regime 1 (low compositional drift, less constrained availability)

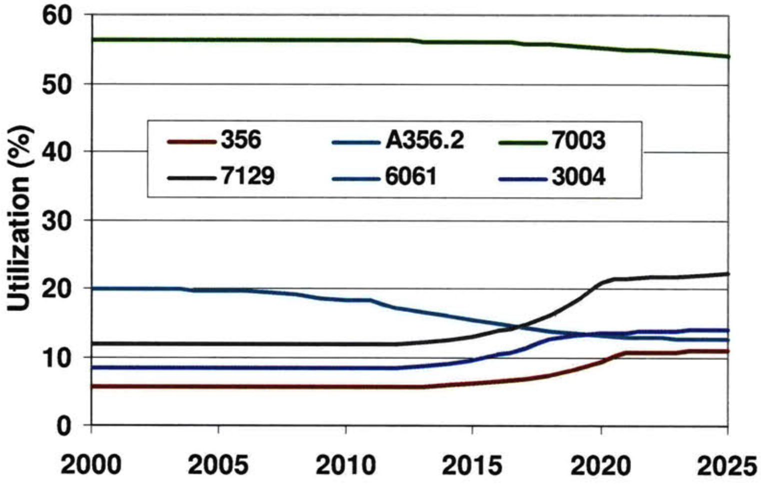


Figure 68. Scrap utilization for selected alloys showing both static and changing allocation

It was hypothesized that this sort of equilibrium or static behavior in the recycling system would result in less of a difference between the time-independent value of the upgrading technologies (sorting and dismantling) and the time-dependent value. Figure 69A supports this hypothesis showing only a slight difference between the snapshot and time-dependent value results; the snapshot results show a 7% higher value for sorting and a 2% higher value for dismantling. These values are calculated by taking the production cost of either sorting or dismantling and subtracting the production cost of the co-mingled case. The time-independent snapshot value is the single period value multiplied by the number of periods considered (26 for this case ie. years 2000-2025). Figure 69B shows how the value changes over time for both technologies, the large dashed line is the average value of the changing time-dependent values while the small dashed line is the time-independent snapshot value.

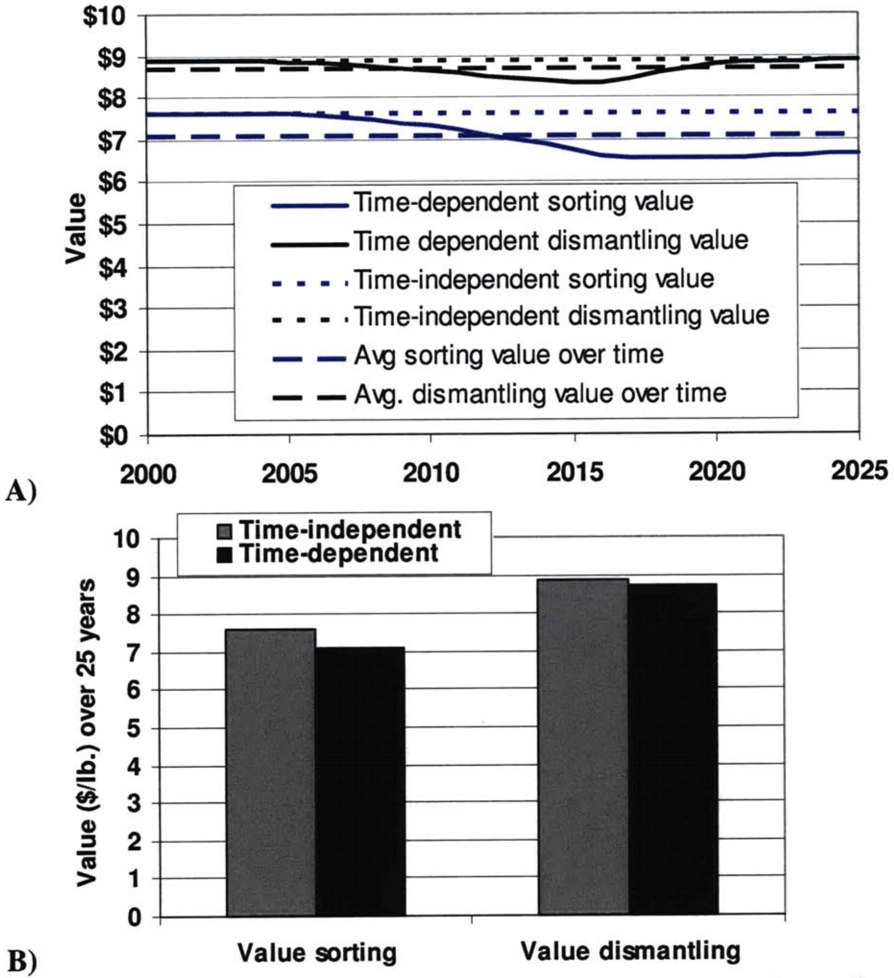


Figure 69. A) The time-independent or snapshot value of sorting and dismantling (specifically, the difference between the cost of having a co-mingled stream and the cost of having a sorted or dismantled stream) compared to the time-dependent multi-generation value for Regime 1. B) Time independent and dependent sorting and dismantling values

Regime 2 still has unconstrained scrap availability but now compositional drift is higher due to additional contamination introduced at end-of-life. One can see that the time-dependent production cost is increasing for all three aerospace end-of-life cases: dismantled, sorted, and co-mingled (Figure 70). This tracks with decreasing scrap utilization for all three cases. Because the availability of scrap is not limited, the amount used will depend on the compositional specifications of the products. End-of-life contamination causes increased compositional drift; over time more of the scrap compositions will reach the maximum specifications for the alloys produced thus capping further usage and resulting in increasing costs over time. Starting out, the commingled stream already is more compositionally constraining than the sorted or dismantled cases due to alloy mixing. Therefore, the end-of-life contamination will cause utilization of the sorted and dismantled streams to drop at a faster rate than the co-mingled stream.

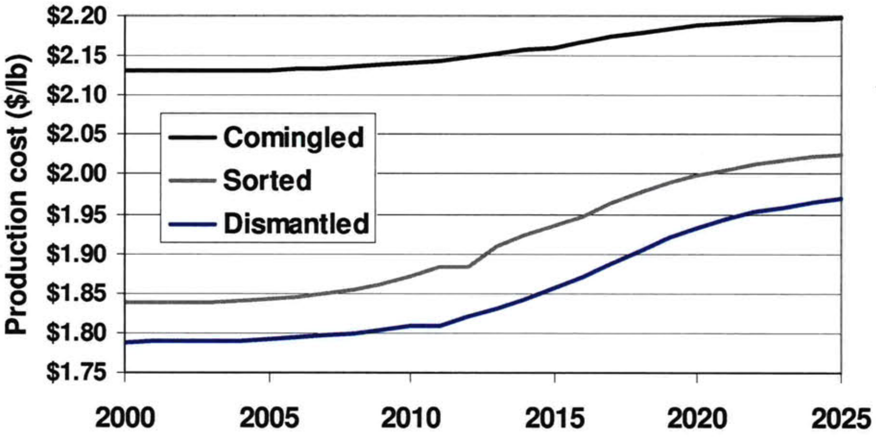
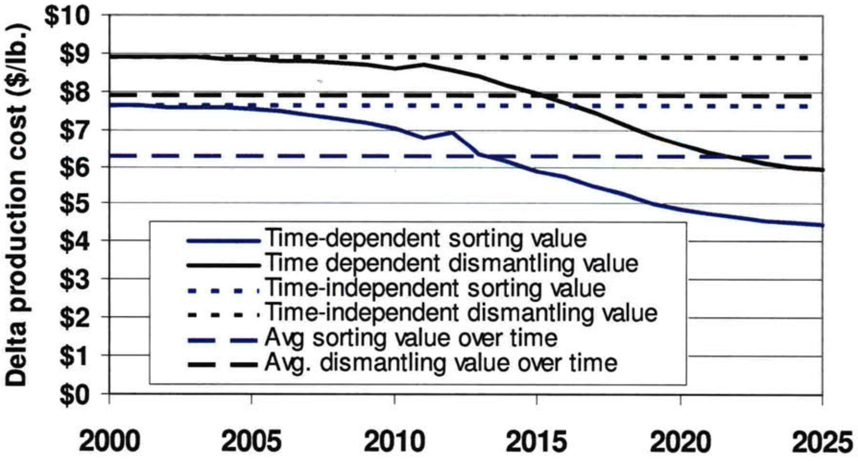
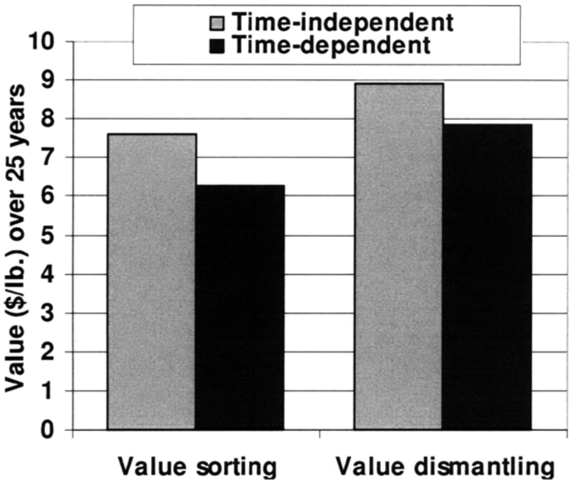


Figure 70. Time-dependent production costs for Regime 2 (high compositional drift and unconstrained scrap availability)

Because the costs for the sorted and dismantled case are increasing at a faster slope than the co-mingled case, the difference between them grows smaller over time. This causes the time-independent snapshot to overvalue both upgrading technologies because the value is decreasing over time (Figure 71B). The time-independent value is 17% higher than the time-dependent multiple generation value for sorting and is 11% higher for dismantling (Figure 71A).

A)





B)

Figure 71. A) The time-independent or snapshot value of sorting and dismantling compared to the time-dependent multi-generation value for Regime 2. B) Time independent and dependent sorting and dismantling values

Regime 3 now has availability that is being determined by the dynamic MFA which considers lifetime of the scraps materials and collection rate assumed for aerospace. In this regime, the compositional drift is less significant due to no additional end-of-life contamination, only changing compositional due to co-mingling or product make-up. Figure 72 shows how the production costs change over time for the three end-of-life cases. Interestingly, the production costs for the dismantled and sorted cases are nearly the same. This is because both cases are availability constrained; all of the available scrap is being used in the production portfolio each year. The co-mingled case however is compositionally constrained, not all of the available co-mingled scrap can be used in the production portfolio due to some of the contained elements being too high to meet specification. Because not much co-mingled scrap is utilized, it is necessary to produce the alloys using primary. This dilution then effects the composition of scrap that is available in later generations (determined by the lifetime). This cleaner scrap can then be better utilized resulting in a decreasing production cost.

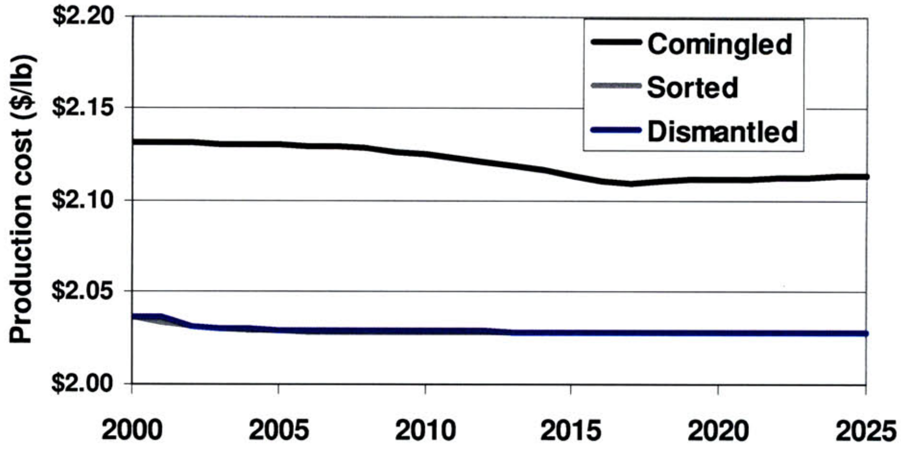


Figure 72. Time-dependent production costs for Regime 3 (low compositional drift and constrained scrap availability)

Because the scrap availability is being determined by the dynamic MFA model, this creates an unfair comparison to the time-independent snapshot which assumed that as much scrap as needed was available to the batch plan. Therefore, the time-independent snapshot was analyzed again, this time with availability constrained to match the results of the dynamic MFA. These are the values (Table XXXV) that will be used to compare to the time-dependent regime 3 case. Because the costs for the sorted and dismantled case are static and the co-mingled case is decreasing for this time period, a time-independent snapshot will again overvalue both upgrading technologies (Figure 73A). The time-independent value is 11% higher than the time-dependent multiple generation value for both sorting and dismantling. One interesting note is that while both regime 2 and 3 overvalue the upgrading technology, regime 2 has much higher values for both technologies compared to 3 (Figure 73B). This would indicate that a compositionally constrained regime would favor the use of upgrading technologies over an availability constrained regime as would be expected.

Table XXXV. Time-independent total production cost and scrap usage for the co-mingled, sorted, and dismantled cases with constrained availability

	Co-mingled	Sorted	Dismantled
Total Cost	$ 3,196.08	$ 3,042.81	$ 3,043.75
Cost/lb.	$2.13	$2.03	$2.03
Scrap usage	252.6	360.0	360.0

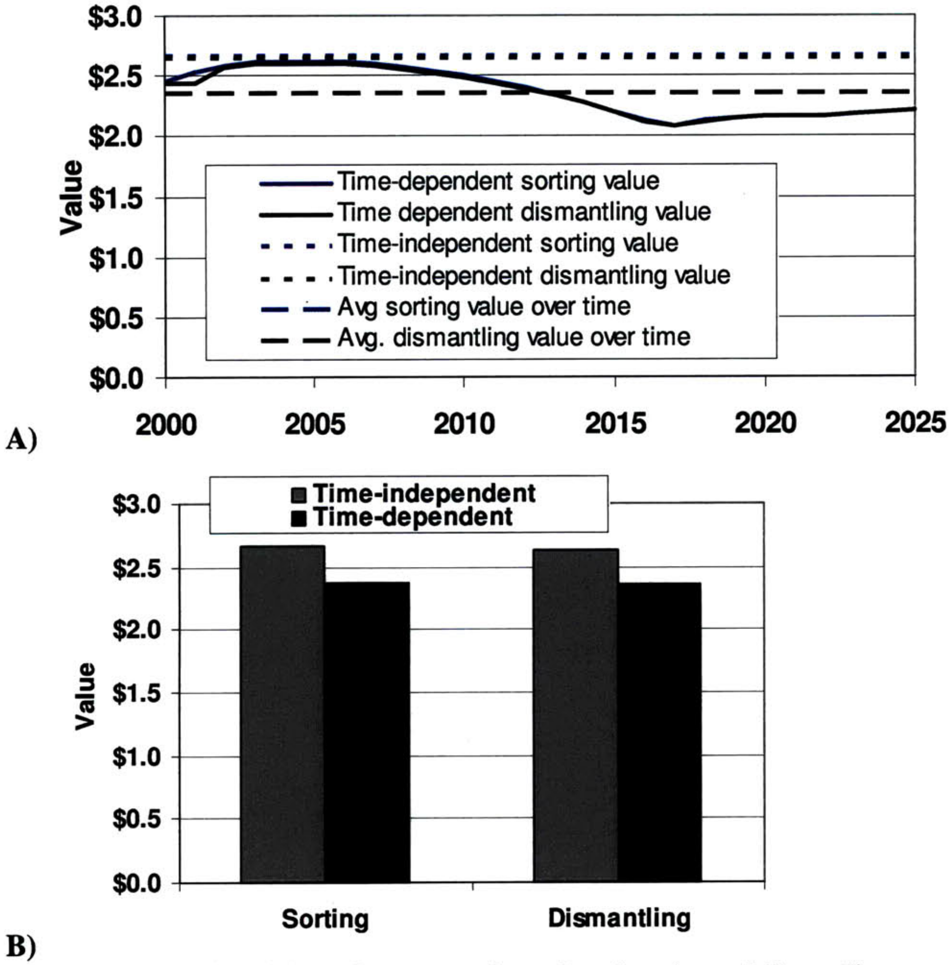


Figure 73. A) The time-independent or snapshot value of sorting and dismantling compared to the time-dependent multi-generation value for Regime 3. B) Time independent and dependent sorting and dismantling values

Regime 4 is where scrap is being determined by the dynamic material flow analysis model and can therefore be constrained by lifetime, collection, and production and compositional accumulation is occurring to a significant degree. It should be pointed out that literature would suggest this regime to be closest to reality for many producers in the US (Sibley, Butterman et al. 1995; Toto 2004). Figure 74 shows how production costs evolve over time for the three cases. As with regime 3, the production costs for the sorted and dismantled case have collapsed to the same cost as their utilization is constrained by availability. The high degree of compositional drift causes the co-mingled stream to become more compositionally constrained over time. This causes a significant drop in utilization and therefore an increase in production cost.

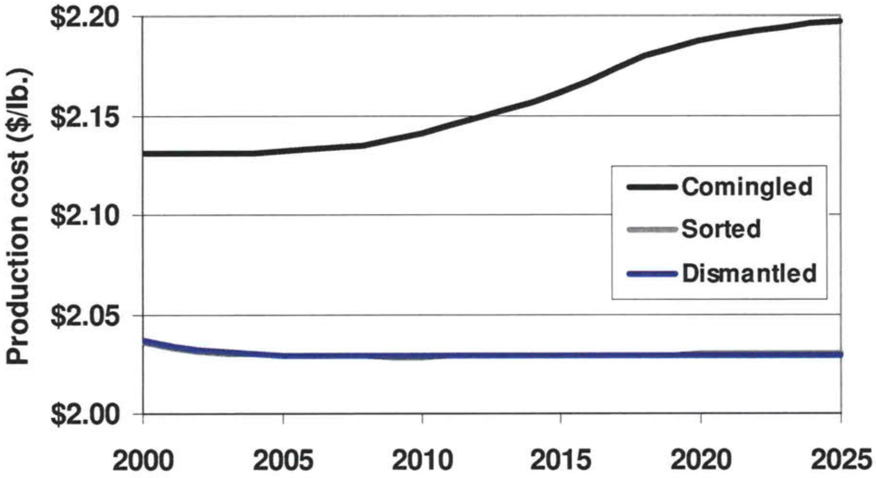
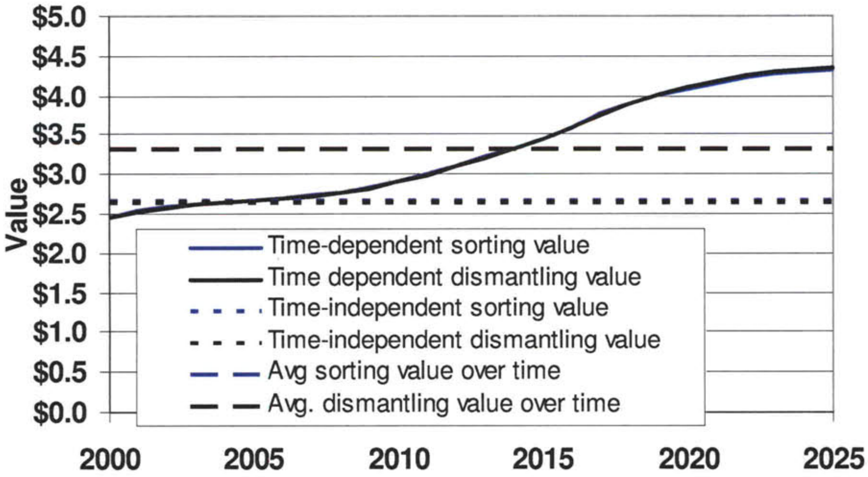
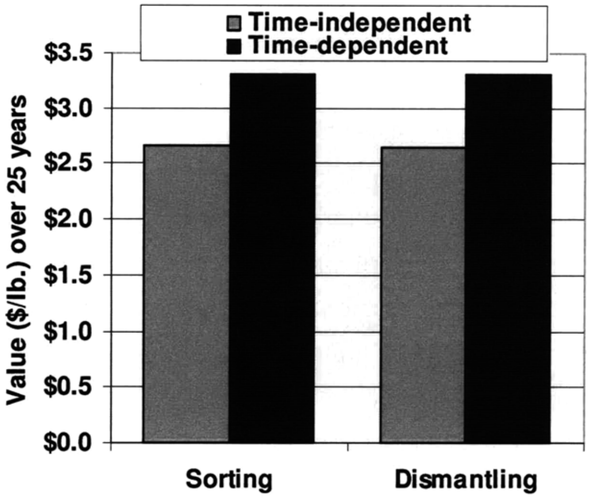


Figure 74. Time-dependent production costs for Regime 4 (high compositional drift and constrained scrap availability)

Because the costs for the sorted and dismantled case are static and the co-mingled case is increasing significantly for this time period, a time-independent snapshot will undervalue both upgrading technologies (Figure 75A). The time-dependent value is 20% higher than the time-independent multiple generation value for sorting and 25% higher for dismantling. This is because initially the values agree quite well (Figure 75B) but over time as the costs are increasing, these upgrading technologies provide a higher and higher value.



A)

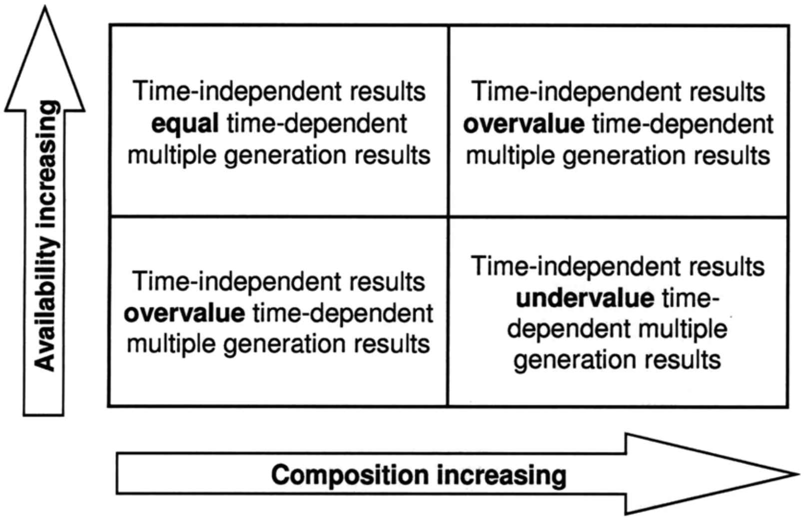


B)

Figure 75. A) The time-independent or snapshot value of sorting and dismantling compared to the time-dependent multi-generation value for Regime 4. B) Time independent and dependent sorting and dismantling values

7.2.3 Summary of sorting and dismantling of aerospace case

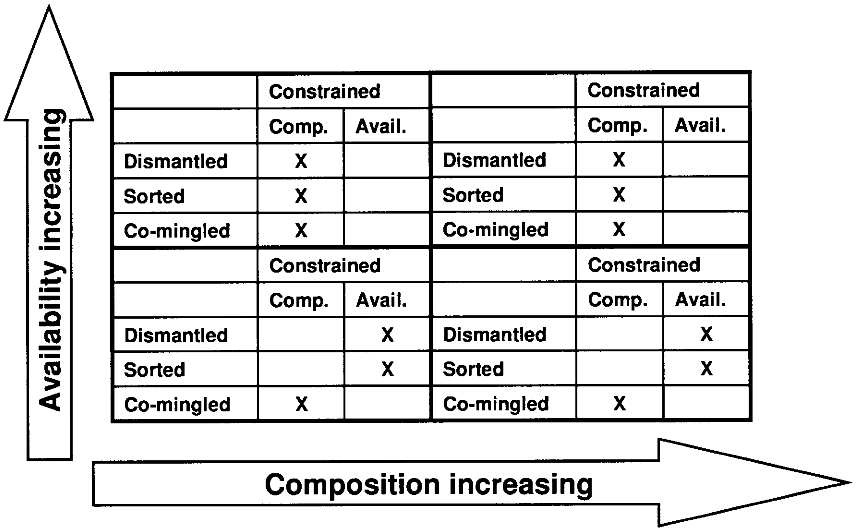
In summary, the difference in value between a time-dependent and time-independent analysis will depend greatly on the availability and composition dynamics present in the recycling system (Figure 76). Four regimes have been identified initially in this work that show both agreement in value as well as over and under-valuing. It should be repeated that for the case of significant compositional drift and constrained availability which may be close to the reality faced by many producers, a time-independent analysis will significantly undervalue both of these technologies.



Time-independent results **equal** time-dependent multiple generation results	Time-independent results **overvalue** time-dependent multiple generation results
Time-independent results **overvalue** time-dependent multiple generation results	Time-independent results **undervalue** time-dependent multiple generation results

Figure 76. Summary of behavior found in four dynamic availability and composition regimes

Figure 77 summarizes whether the utilization of each of the three end-of-life scrap streams is availability or compositionally constrained in the regimes examined. In the abstract, one could envision two other regimes as well, one in which no scrap can be used (i.e. the alloys are made entirely of primary and alloying elements) and one in which production is made entirely of scrap (no dilution or addition is necessary to meet specification). In the regime where production consists entirely of scraps, there would be no availability *or* compositional constraints. In the regime where no scrap could be used, either no scrap is available for use (all three are availability constrained) or the scraps would all be compositionally constrained. Neither of these regimes are likely for the entire production portfolio under actual operating conditions. However, there are certainly some specific products that have extremely high scrap utilization (>90%) such as castings and aluminum that goes into steel deoxidation as well as many products that require that no scrap materials be used such as aerospace and superconductors.



	Constrained			Constrained	
	Comp.	Avail.		Comp.	Avail.
Dismantled	X		Dismantled	X	
Sorted	X		Sorted	X	
Co-mingled	X		Co-mingled	X	

	Constrained			Constrained	
	Comp.	Avail.		Comp.	Avail.
Dismantled		X	Dismantled		X
Sorted		X	Sorted		X
Co-mingled	X		Co-mingled	X	

Figure 77. Summary of constraints controlling scrap utilization in four identified behavior regimes

7.3 Fractional crystallization

7.3.1 Review of time-independent results

The same methodology as described for the sorting and dismantling of aerospace scraps was used for the fractional crystallization case. The production portfolio was altered slightly from the case presented in chapter 5 and includes the alloys listed in Table XXXVI. Alloy 5182 is an addition that was not included in chapter 5 (specifications shown in Table XXXVII); this is due to the fact that considering multiple generations requires some matching between the scrap and production portfolio in order for the composition of the products to become the composition of the scraps in future generations; 5182 prompt scrap was considered in the case presented in Chapter 5 but 5182 finished alloy was not part of the production portfolio.

Table XXXVI. New reduced production portfolio for fractional crystallization case

High Tech	Low Tech
Electrolytic Cap Foil -1	5182
Electrolytic Cap Foil -2	3004
AA1050	6061
AA1060	356
AA8011	5052
Disk Blank CD1	2014
Disk Blank PD2	4045
Disk Blank CD2	7005
Disk Blank AD2	2014

Table XXXVII. Maximum and minimum specifications (weight fraction) for alloy 5182 added to the product portfolio for the fractional crystallization case

	Si	Mg	Fe	Cu	Mn	Zn
Max	0.002	0.5	0.0035	0.0015	0.005	0.0025
Min	0	0.4	0	0	0.002	0

The altered production portfolio combined with the mean-based method will result in slightly altered values for cost savings from those presented in Chapter 5. All other parameters (scrap composition, product specifications, and price) are the same as the case presented in Chapter 5 (cf tables). One can see that this slightly altered production portfolio results in the same trend as shown previously (Figure 78); that the maximum savings are realized early on in the refining process (when less of the total amount of scrap is upgraded). How the value of this technology changes over time will be examined in the next section.

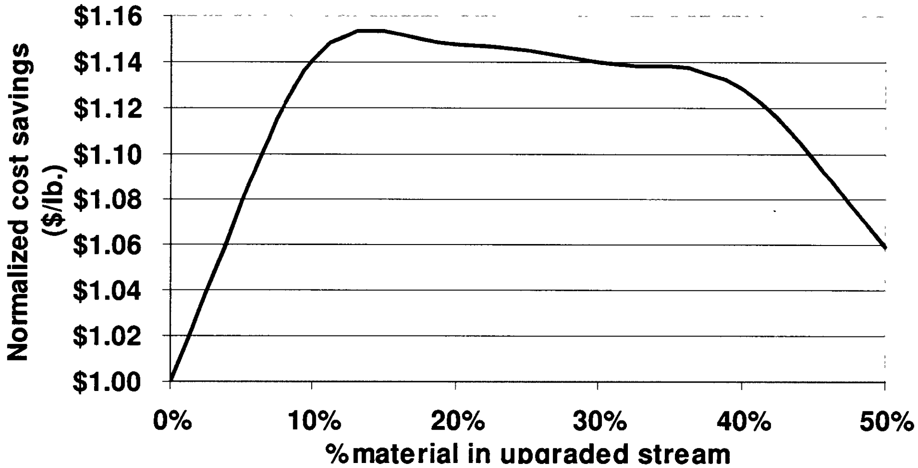


Figure 78. Time-independent normalized cost savings with increased refining (i.e. percentage of material in the upgraded material stream)

7.3.2 Time-dependent value of fractional crystallization

For this analysis, the dynamic material flow analysis combined with blending was used to investigate the value of fractional crystallization (parameters as listed in chapter 5) as an upgrading strategy. The scrap materials were assumed to be prompt scrap and therefore had a one year lifetime with no deviation; this ensures that the scrap material will be available in the time period directly following its production. Because of this prompt scrap assumption, only the prompt scrap rate in fabrication will determine the availability of the scrap stream as opposed to lifetime and collection for the sorting and dismantling case study shown previous. For the fractional crystallization case, the degree of refining determines the amount of upgraded material available and this will be the main availability leverage point. Because of this, the degree of refining will be explored across the entire range for the other two regimes: low and high compositional drift.

The same five scrap cases analyzed for the time-independent value were used for this analysis as well as shown in Table XXXVIII. The composition of the alloy produced will become the scrap for the next year if there is no refining done to it. For refining, it is assumed that the scrap stream will undergo the fractional crystallization process to a certain degree resulting in a downgrade and upgrade stream, described in detail in chapter 5. The downgrade will collect the tramp elements removed from the purified upgrade stream according to the multipliers calculated in chapter 5.

Table XXXVIII. Alloy produced and resulting scrap to be upgraded or downgraded

Scrap case	Alloy produced
5182 scrap	5182
UBC	3004
Wrought extrusions	6061
Mixed castings	356
Base case Alcoa study	5052

It is assumed that an equal amount of each of the alloys in
Table XXXVI will be produced and this production will stay static over time. Figure 79 shows the production cost over time for various degrees of refining in the fractional crystallization process (0% is no refining). This degree of refining is equivalent to the percentage of material that ends up in the upgraded stream, i.e. the further you refine, the more purified scrap material available. Because lifetime and changing production volume are not significantly affecting the scrap availability, the system reaches a steady state quite quickly where the costs level out. This is because all of the available scrap is being used every year. The introduction of a new technology results in the initial transient behavior as the secondary producers in the system would readjust their

production portfolios according to the resulting differing compositions due to using this upgrading technology.

As the refining process progresses, more and more of the scrap stream will be upgraded and downgraded until it reaches 50% which is as far as refining can go; this indicates that the scrap stream is now 50% upgrade and 50% downgrade. The production cost is decreasing for the increasing degrees of refining because scrap utilization is increasing as more and more purified scrap material is created. However, having steady costs and overall scrap use does not mean that other factors are not changing. The optimal allocation will choose different products to put the available scrap material into depending on the alloying element content within the scrap. Figure 80 shows the percentage of scrap in five different alloy products illustrating the changing allocation over time.

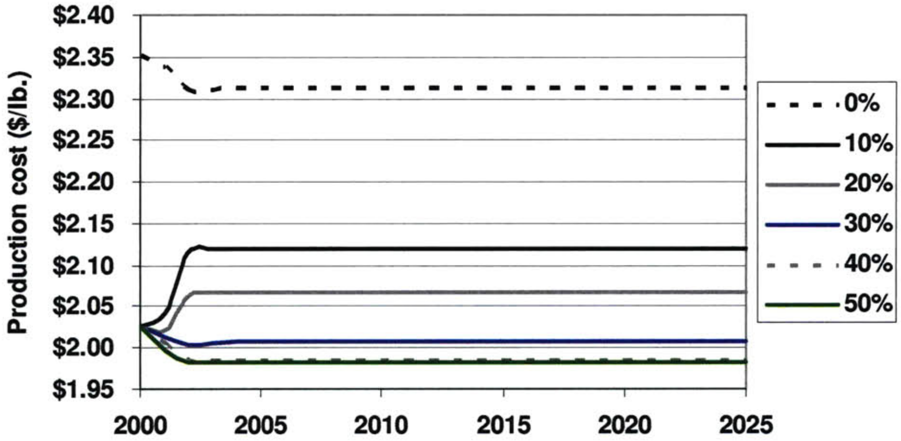


Figure 79. Production cost over time for no fractional crystallization (0%), and various degrees of refining

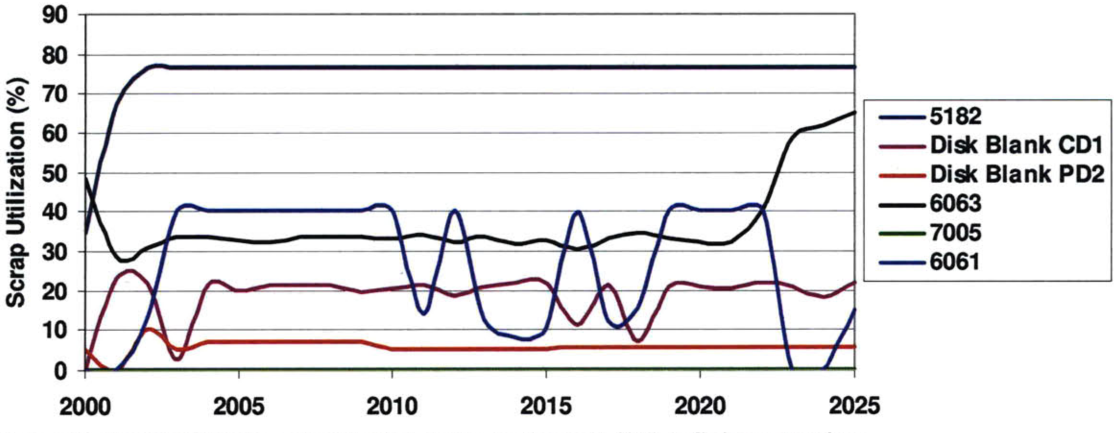


Figure 80. Scrap utilization for selected alloy products at 40% refining over time

To compare these results to the time-independent analysis, it is easier to look at the production costs for each year shown in Figure 81. One can see that the first year this upgrading technology is introduced (year 2000, the solid black line), the costs for each degree of refining show similar behavior to the time-independent results (cf. Figure 78). However, over time, there is no longer a minimum in the cost savings, further refining results in decreased costs. This is because purifying the scrap stream early on will result in keeping utilization high in future years. So not only does the time-independent result undervalue the fractional crystallization technology overall but it would also indicate that less refining is actually optimal in terms of cost savings. If only a small amount of refining is done at each period, this would result in sub-optimal future scrap use according to the time-dependent analysis.

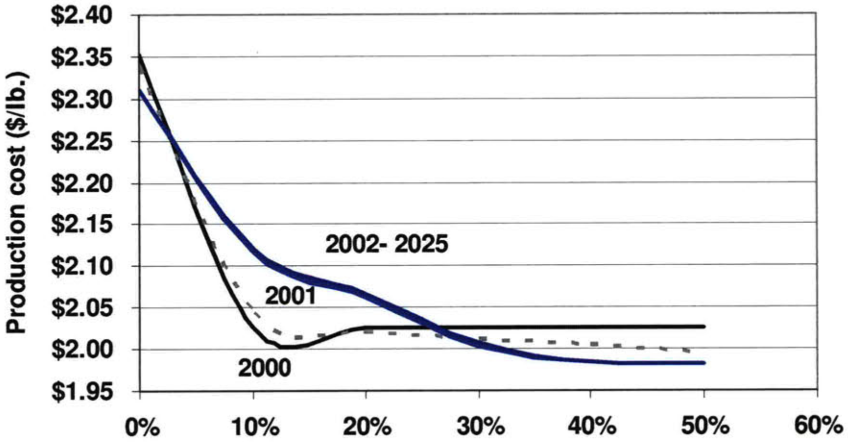


Figure 81. Same data as Figure 79 (production cost over time at various degrees of refining) but plotted for each year: black line is year 2000, dotted gray line is year 2001, and years 2002-2025 have the same blue cost curve

7.3.3 High compositional drift -accumulation

As detailed previously, the static scrap availability results in compositional drift being the main leverage point in terms of different regimes of behavior for this case within the aluminum recycling system. Increasing compositional drift, regime 4 from Figure 63, will be examined in this section for fractional crystallization. Increased compositional drift or accumulation in this regime is due to contamination or pick-up that happens beyond typical co-mingling and product mixing accumulation. For this analysis, a contamination ratio of 1 was used which is still quite conservative in regards to actual operating conditions. Using a ratio means that scraps that typically have higher amounts of certain elements present will increase more while scraps that are typically quite clean will not change significantly. As an example, if there was a scrap stream with 0.5 wt. % zinc in it, an accumulation ratio of 1 would mean that the new composition would be 1 wt. % zinc. For a scrap stream with a high quantity of silicon present like castings, a contamination ratio of 1 would result in a 5 wt. % composition to increase to 10 wt. %.

Circumstances that would cause contamination ratios above 1 for example would be if a steel screw ended up in the aluminum scrap stream or if aluminum-copper radiators ended up in automotive shred. Physical examples of lower contamination ratios would be iron pick-up from processing equipment such as shredding or silicon pick-up from melt refractories.

Figure 82 shows how the production cost will change over time for various degrees of refining, now considering increased compositional drift or accumulation. One can see that these costs are higher than in Figure 79 because this high compositional drift will drive up tramp element content in the scrap stream thus limiting utilization. A high contamination ratio means that utilization will shift from being availability constrained to compositionally constrained. This occurs in particularly for the downgraded portion of the refined scrap material. The amount of elements within the downgraded scrap will be increasing due to the refining process itself, high compositional drift will compound this problem. Figure 83 shows the magnesium and manganese composition of the downgrade portion of some of the scraps, an example of this increase. These compositions will increase until several of the maximum specifications for magnesium and manganese are reached for the alloys being produced. This will restrict the amount of downgrade that can be utilized, thus driving up the production costs. This creates an even larger gap between the first tracked year's costs and the equilibrium costs for the following years (Figure 84).

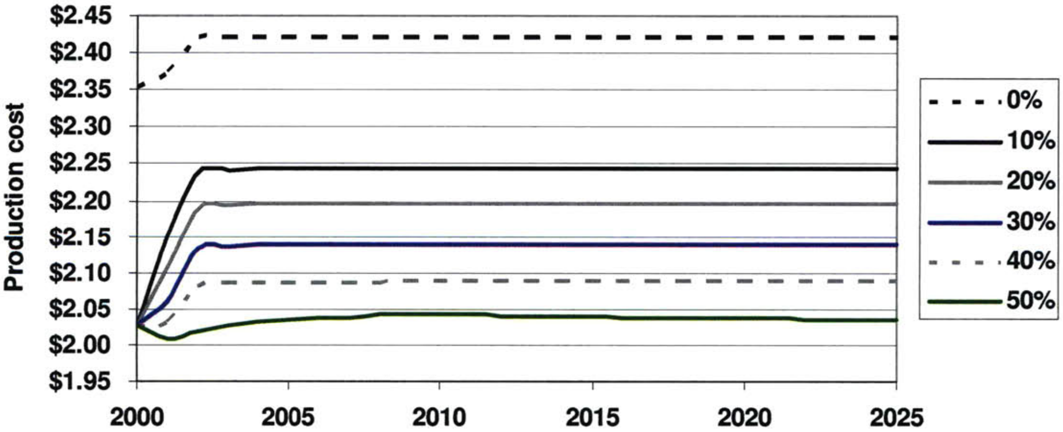


Figure 82. Production cost over time for no fractional crystallization (0%), and various degrees of refining with additional contamination

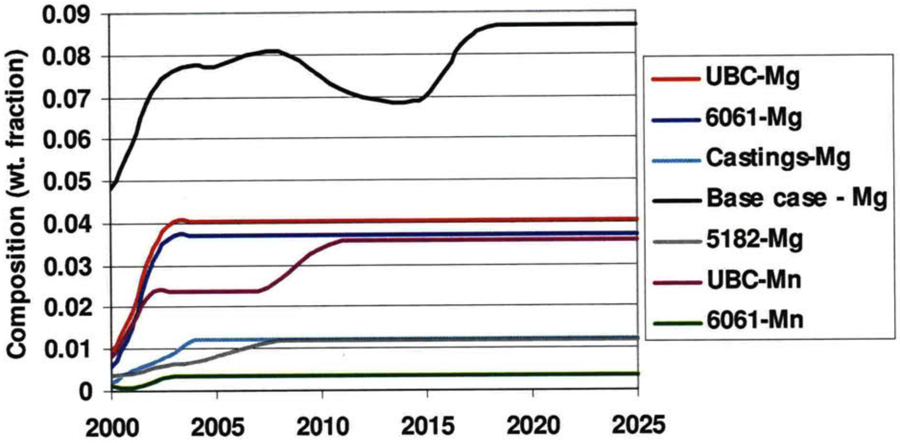


Figure 83. Compositional drift over time for downgraded portion of some of the scrap cases

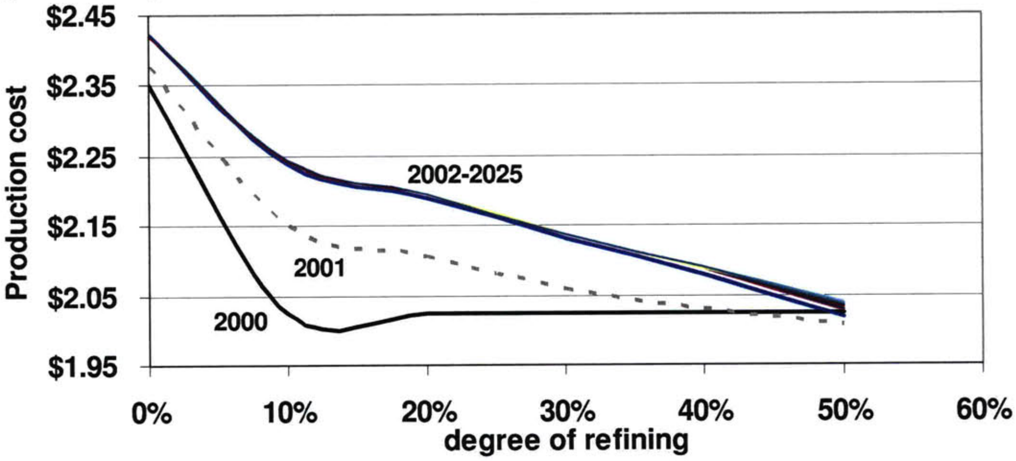


Figure 84. Same data as Figure 82 (production cost over time at various degrees of refining) but plotted for each year

7.3.4 Summary of time-dependent value of fractional crystallization

Figure 85 shows the normalized value of fractional crystallization at various degrees of refining within the process as compared to no refining (having the base case scrap available for use in the product portfolio). Figure 86 summarizes the results for the four main regimes of constrained availability (degree of refining for this case) and constrained composition. One can see that the time-independent analysis indicates a higher value to stopping the refining process early on as well as slightly undervaluing the technology overall in terms of maximum savings possible. Not only does the time-dependent analysis not show a maximum value in refining only to a certain degree but it also shows that just using the base scrap would actually result in a lower production cost than doing only a little refining. This is because the upgraded stream has not been purified far enough to ensure increased usage in future years while the downgrade will continue to become poorer in compositional quality with repeated recycling. This effect is compounded by higher compositional drift caused by contamination and pick-up. However, when considering contamination, a slightly larger value is seen at 50% refining compared to the time-dependent analysis and the time-independent analysis with less significant compositional drift. This would indicate that when a producer is faced with high contamination or pick-up, the fractional crystallization technology would provide an even higher value to them over time.

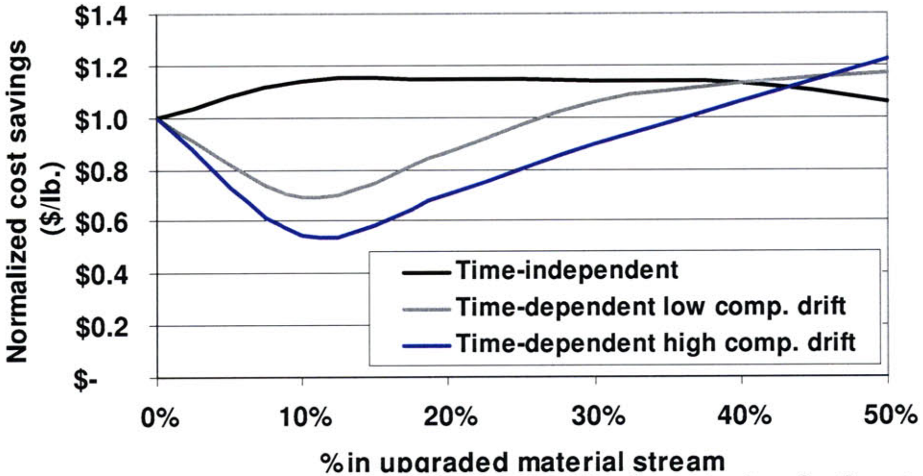
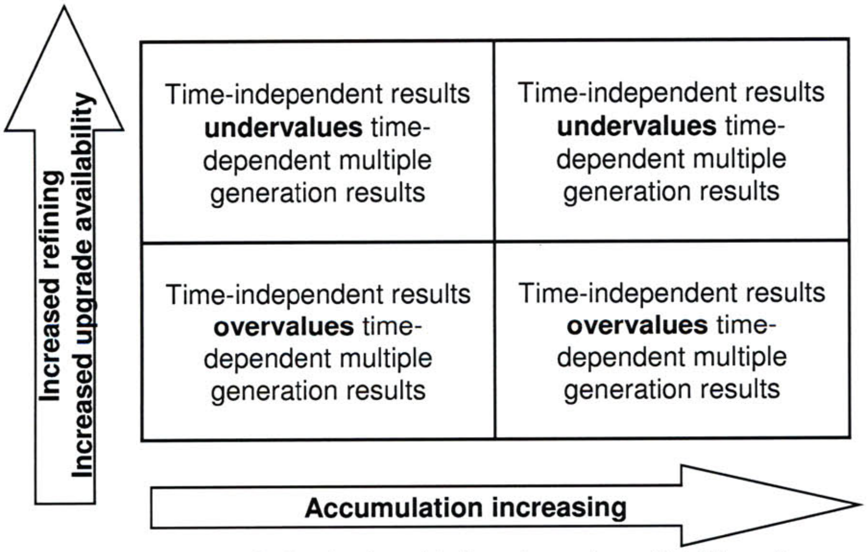


Figure 85. Normalized cost savings of fractional crystallization technology for three types of analysis: time-independent snapshot, time-dependent analysis with low and high compositional drift



Time-independent results **undervalues** time-dependent multiple generation results	Time-independent results **undervalues** time-dependent multiple generation results
Time-independent results **overvalues** time-dependent multiple generation results	Time-independent results **overvalues** time-dependent multiple generation results

Figure 86. Summary of behavior found in four dynamic availability and composition regimes for the fractional crystallization case

7.4 Summary of time-dependent value of upgrading cases

The cases of sorting, dismantling, and fractional crystallization would indicate that the methodology developed in this thesis is a capable framework for evaluating the time-dependent value of upgrading technologies. This framework could be used to evaluate other technologies detailed in chapter 4 as well as provide preliminary indication for the value of technologies still in the research and development phase. If the relevant data were available such as product lifetimes and demand, scrap collection, and compositional break-downs; this methodology could be extended to other recycled material streams as well.

Initial results for a physical separation and refining technology would indicate that the value of these technologies relies heavily on the constraints imposed by parameters controlling the material flows in the recycling system. Specifically, whether or not the scrap stream is compositionally or availability constrained can have a large impact on the value of both operational and technological strategies for increasing recycled material usage.

Chapter 8. Conclusions

As consumption of materials in the United States grows, so does concern about sustainable materials usage. Increasing recycling, or the use of secondary materials, is a key component within a broad arsenal of strategies for moving towards sustainable materials usage. This is because, in most cases, the usage of secondary resources requires significantly less energy than manufacturing products purely from primary resources. This is especially the case for aluminum whose growing rate of consumption combined with these significant energy savings motivates its use as a case material; increasing effective aluminum recycling has a potentially large environmental impact.

There are many barriers to increasing recycling as outlined in this thesis; one of the most problematic is uncertainty, specifically, uncertain demand, availability, price, and composition. Uncertainties will affect the decisions that secondary producers must make, specifically, their blending, or batch-planning decisions. These uncertainties must be taken into consideration when making the decision of what mix or blend of these materials they will select to create their production portfolio or batch-plan. Despite real uncertainties in each of these parameters, these decisions must be made on a daily basis.

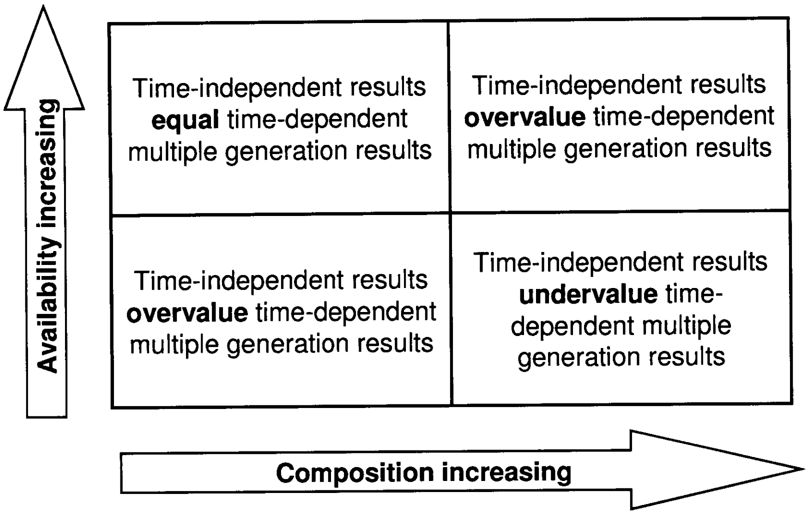
One of the key uncertainties that materials engineers are uniquely positioned to address is compositional uncertainty in the scrap stream. Compositional uncertainty presents a major barrier to the increased usage of recycled materials; repeated recycling compounds this problem through the accumulation of tramp elements in the recycled material stream. This accumulation is a time-dependent process based on this repeated recycling over multiple scrap generations. There are a variety of operational and technological strategies that exist to mitigate accumulation. It was hypothesized that optimal allocation of scrap materials was one such operational strategy. As important as these types of operational strategies are to mitigating the negative effects of accumulation, there are far more technological strategies available to the producer when these operational strategies become ineffective. These upgrading technologies were described in chapter 4, categorized by the main mechanism in which they remove unwanted elements either by 1) physically separating solid scrap streams to prevent co-mingling of metals and elements or, 2) refining technologies that attempt to chemically or kinetically move unwanted particles and elements in the melt. Pertaining to these available technologies, one would want to know: 1) How effective are operational or technological strategies at mitigating accumulation? 2) Under what conditions do upgrading technologies provide a cost-efficient and environmentally effective improvement to the composition of recycled scrap streams? The wide variety of technological strategies that are available suggested that a tool for valuation is essential.

In order to answer these questions about upgrading, this tool required characteristics capturing 1) the flow of end-of-life scrap materials, 2) a method to evaluate how the economics of production are affected by changes in technology, and 3) a characterization of how recycling parameters influence accumulation in recycled streams. Previous literature has used methods which individually address either 1) dynamic material flow analysis, or 2) optimal batch planning or blending, but not their combination. This thesis addressed this gap by combining dynamic material flows analysis comprehending end-of-life materials with optimal allocation of those materials into production portfolios using blending models. The dynamic MFA portion will allow the inclusion of compositional details for end-of-life aluminum scraps in the United States broken down by alloy. The inclusion of blending models allow the incorporation of agency within the MFA framework, specifically, how the recyclers as stakeholders can influence the behavior of the system. These models also allow an understanding of the economic value of changes in technology and scrap composition. Most importantly, the inclusion of batch planning captures another operational solution: optimal allocation of recycled scrap materials.

First, a time-independent, snapshot analysis was conducted for two upgrading cases: dismantling, sorting, and shredding of aerospace scraps and fractional crystallization of co-mingled scraps. Results showed that dismantling and sorting can provide cost savings through increased aerospace scrap utilization when compared to shredding (co-mingled scrap stream). This improvement was shown to be heavily dependent on the amount of uncertainty in the scrap composition and therefore the efficiency and accuracy of the technology in question. For example, the sorted case would need to yield compositional coefficients of variation less than 20% in order to provide significant savings over the co-mingled case. Fractional crystallization results suggest that the technology achieves maximum benefit after only limited refining, at approximately 20% upgrade yield, and the value is strongly dependent on the specifics of the raw material to be upgraded. The equilibrium distribution coefficients would indicate that scrap streams high in silicon and iron would see the most benefit from this type of upgrading technology; results shown in chapter 5 support that conclusion.

It was hypothesized that the time-independent value of upgrading will equal the time-dependent value if the behavior of the recycling system is static, ie. there are no transient or dynamic behavior present. Chapter 6 explores the impact of dynamic elements present in the aluminum recycling system, focusing on composition and availability. Factors influencing scrap availability are production, collection, and product lifetimes. Increasing production or demand means that there is comparably less scrap material available. Increasing collection rates will increase the scrap availability. Longer product lifetimes can constrain availability by shifting forward the time in which the end-of-life materials will be collected. The composition of the scrap stream can change due to differing batch plans from generation to generation as well as the mixing of materials to create products. More significant compositional drift will occur when there is additional pick-up or contamination from end-of-life processing or co-mingling or differing products and scrap types (composition increasing). Using this time-dependent methodology, compositional drift within the recycled scrap stream was compared with and without optimal allocation. Without batch planning, the composition of the scrap stream is determined only by statistics for the above parameters. Optimal allocation was found to be an effective strategy for mitigating accumulation, for example, the level of iron in the scrap stream was 69% less when compared to the statistical value.

The cases of 1) sorting, dismantling, and shredding of aerospace scraps, and 2) fractional crystallization of co-mingled scraps, were examined again using the methodology combining dynamic material flow analysis and blending models. This methodology was proven to be a capable framework for evaluating the time-dependent value of upgrading technologies. Initial case results would indicate that the value of these technologies relies heavily on the constraints imposed by parameters controlling the material flows in the recycling system. Specifically, whether or not the scrap stream is compositionally or availability constrained can have a large impact on the value of both operational and technological strategies for increasing recycled material usage. Figure 76 reiterates the results from the shredding, sorting, and dismantling of aerospace scraps case. Depending on the regime, a time-independent snapshot can equal, overvalue, or undervalue the upgrading technology in question. Results indicate that undervaluing will occur in a regime where scrap availability is constrained and there is significant compositional accumulation occurring, a regime that may very well represent the reality faced by aluminum secondary producers in the US. Overall, the value of upgrading technologies was much higher in this regime. This would indicate that a compositionally constrained regime would favor the use of upgrading technologies over an availability constrained regime, a useful rule of thumb for producers.



Time-independent results **equal** time-dependent multiple generation results	Time-independent results **overvalue** time-dependent multiple generation results
Time-independent results **overvalue** time-dependent multiple generation results	Time-independent results **undervalue** time-dependent multiple generation results

Figure 87. Summary of behavior found in four dynamic availability and composition regimes

Finally, it is important to note that these models are still simplifications of the large, complex, and dynamic aluminum recycling system. As such, there are many other aspects left unexplored by these analyses. An introduction to these aspects is provided in the future work section.

Chapter 9. Future Work

9.1 Limitations of current work

The cases chosen for this analysis show that the methodologies developed are quite effective for exploring the time-dependent value of upgrading. However, the regimes of constrained availability and composition explored within these two cases may not reflect the entire decision space; for example, regimes most likely exist with fully constrained availability which were not found in this case (cf. Figure 77). Also, the cases explored may be limited in their scope, both in terms of the technology explored, and the case scraps selected.

Though the methodology developed in this thesis to explore the time-independent and dependent value of upgrading technologies provides a significant contribution, one key limitation still exists: a single stakeholder perspective.

9.1.1 Exploration of regime extremes

For the aerospace case, one could envision two regimes not explored in the analysis in chapter 7, one in which no scrap can be used (i.e. the alloys are made entirely of primary and alloying elements) and one in which production is made entirely of scrap (no dilution or addition is necessary to meet specification). In the regime where production consists entirely of scraps, there would be no availability *or* compositional constraints. In the regime where no scrap could be used, either no scrap is available for use (all three are availability constrained) or the scraps would all be compositionally constrained. Under actual operating conditions, specific products can have extremely high scrap utilization (>90%) such as castings and aluminum that goes into steel deoxidation. Other products may require that no scrap materials be used such as superconductors. An exploration of these regimes may therefore yield interesting results that could impact secondary production.

9.1.2 Extended cases

The cases selected for this analysis may be limited in scope. For the case of dismantling, sorting, and shredding of aerospace scraps, while the technology is broadly applicable, aerospace may be a limited scrap set. These scraps are not currently being recycled to a large extent and they make up a small portion of the transportation sector within the overall aluminum end-use shipments. For the case of fractional crystallization, while both the scrap and production portfolio are quite broad and reflect much of the current aluminum market, the technology is quite limited. Fractional crystallization has been accomplished only at the research and development level and has had limited application to industrial scale refining. The wide array of upgrading technologies explored in chapter

4 would indicate a rich research space for examining other types of upgrading technologies using the methodology developed in this thesis. The wide range in scrap types and finished alloys produced, as described in chapter 6, would also indicate that many unexplored case parameters exist. Modifications such as the addition of thermodynamic data or extension to other properties of interest such as mix viscosity would enable this methodology to be extended to other recycled material streams as well.

9.1.3 Stakeholders

One limitation of this methodology is the single stakeholder perspective, namely that of the secondary producer. In actuality, there are many stakeholders within the recycling system. Figure 88 shows the schematic of major flows within the system now indicating the relevant stakeholders. The blending program within the methodology could be used to optimize the system according to the material producer's (base case shown in this thesis), the recyclers or scrap collectors, the consumer, or the OEM's who purchase the finished alloys. If the computational complexity allowed, the system could be optimized as a whole as well. This would represent stakeholders such as major industry associations such as the Aluminum Association and the International Scrap Recycling Institute. Government bodies such as legislators, municipalities, or the US Geological Survey could also benefit from understanding the value of upgrading technologies and the economics of the recycling system as a whole.

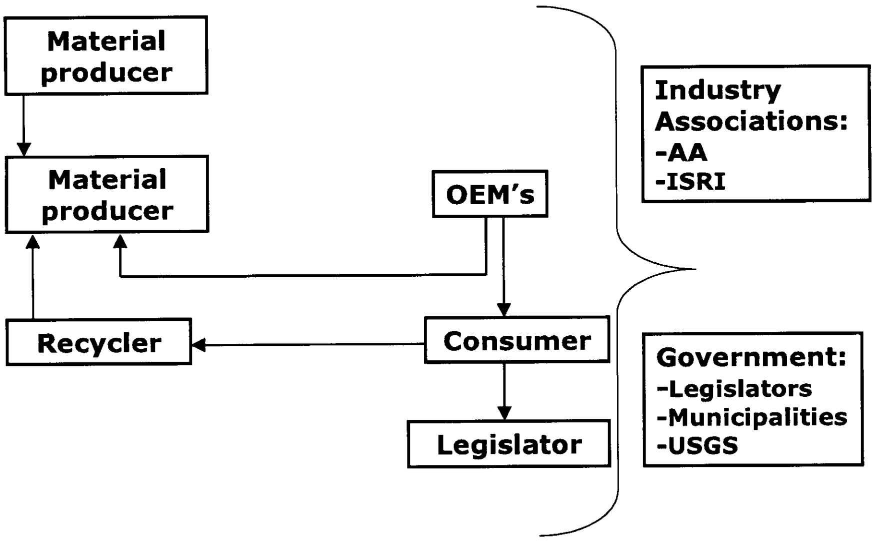


Figure 88. Schematic of stakeholders within the recycling system

9.2 Long-term research plan

One of the key engineering challenges of the 21st century will be reducing the harmful effects associated with a growing population and the attendant flows of materials(Graedel and Allenby 2003). The materials community is uniquely positioned to play a central role in addressing these problems by fundamentally changing the materials and processes used by society. For this to happen, materials experts must begin to consider the environmental impacts of their design choices and will require additional analytical tools to quantify those broader implications. My research work begins to address this need by examining the environmental and economic impacts of material and materials technology decisions. More specifically, I envision my research focusing on increasing materials recycling through the following operational, technological, policy, and manufacturing strategies:

Extensions of current work:

- creating economically efficient usage strategies
- evaluating effective technologies for "upgrading" secondary materials

Long-term research vision:

- designing and selecting recycling-friendly products
- identifying and removing barriers and disincentives to secondary usage
- enabling efficient collection and logistics
- identifying undervalued secondary materials
- preventing "down-cycling" through improved recycling operational practices
- informing recycling system legislation and policies

To guide technology decisions in any of these directions, it is necessary for engineers to be able to analytically evaluate their economic and environmental implications. As these implications will affect a number of stake-holders throughout the process chain, this analysis will require a systems engineering approach.

9.2.1 Identifying and Removing Barriers to Usage: Dealing with Uncertainty

- How does the level of variance in scrap stream composition effect production costs?
- Can compositions of scrap streams be characterized more effectively?
- Does demand side uncertainty (which and how much product to manufacture) or supply side uncertainty (composition, availability and price of materials) have a larger adverse effect?

A significant set of economic disincentives emerge due to the various types of operational uncertainty that confront secondary processors (Peterson 1999; Rong and

Lahdelma 2006). In particular, depending on where one is in the production chain, business-critical sources of uncertainty include capricious demand, unstable availability of raw materials (particularly scrap materials), the precise composition of those raw materials, and the cost of factor inputs. These uncertainties have the largest adverse effect on those furthest from the customer, e.g. materials producers, due to the feedback mechanisms inherent to typical market-based supply-chains (Lee, Padmanabhan et al. 1997). Managing these uncertainties will require improved characterization of scrap composition and variance; this can be accomplished through statistical analysis and probabilistic modeling. Fluctuations can then be tested with this model to evaluate the resulting effects on production cost and scrap utilization. This work can be extended to other sources of uncertainty by creating models that make use of forecasting techniques for customer demand and scrap supply.

9.2.2 Designing and Selecting Recycling Friendly Products

- Which products provide issues and/or opportunities in regards to increased scrap consumption potential?
- How will the incorporation of recycled materials affect the performance of finished products?

The primary challenge in evaluating a product's recycling-friendliness is that it is a context dependent property; how much scrap a product can accommodate will be based on not only the compositional characteristics of the product itself, but also the types of scraps available to producers, the compositional characteristics of those scraps, and their yields. As a result, a method to evaluate recyclability must be able to account for the confluence of these detailed effects. Previous work utilizes a chance-constrained based optimization method to explore the effects of strategic alloy choice in aluminum production on the ability to utilize secondary materials in the alloy's raw material portfolio. Two cases were examined to demonstrate the model's ability to both directly evaluate the recyclability of specific alloy formulations and proactively identify the most effective alloy modification strategies that can drive increased recycling.

Industry experts and literature have provided a variety of other suggestions to increase a product's ability to accommodate secondary materials including higher maximum compositional specifications for certain elements that will not adversely affect product properties, wider specification targets (i.e. higher maximums and lower minimums), or translating compositional constraints to specifications based on performance(Das 2006). Other suggestions involve modifying forming and joining, for example, replacing conventional welding with mechanical joining, laser welding, or friction stir welding(Sutherland, Gunter et al. 2004). Some even propose legislation or regulations to limit the number of alloys that can be used in certain products such as cars or aircraft(Woodward 1997). The model previously developed can be extended to provide a quantitative assessment of the efficacy of these suggestions on the ability of a recycler or recycling system to use more secondary raw materials as well as to which products they should be applied.

9.2.3 Enabling Efficient Collection and Logistics

- How should the physical architecture of a recycling system be configured to ensure optimal participation?
- How greatly does the transport of some scrap materials erode the environmental benefits of their recycling?

The goal of a recycler, whether they be a firm or a municipality, is to maximize the amount of waste collected while minimizing the costs of collection and processing. These costs will rely heavily on any number of factors including population, geography, labor costs, participation levels, etc. In many cases, especially for heavy and/or high volume secondary materials, transportation will be a dominant factor. As the transportation portion of these costs has its own environmental burden (in the form of fossil fuel usage and emission), it is important to consider the implications on the systems benefits as a whole. It is hypothesized that balancing logistics, value, and availability of multiple varying secondary streams will yield many more materials system engineering questions.

9.2.4 Creating Economically Efficient Usage Strategies

- What compositional components are the most limiting in terms of increased usage?
- Can we develop simple metrics to characterize efficient resource use?
- How does the volatility of scrap markets effect operational planning in secondary production?

My dissertation work has shown it is possible to increase the use of recycled material without compromising the likelihood of compositional or performance errors, when using more advanced analytical mixing strategies compared to current practice(Gaustad, Li et al. 2007). This improvement is especially beneficial as computational modifications require little to no capital investment in equipment and space. The strength in computationally modeled usage strategies for secondary materials is time and money saved. For example, sensitivity analysis of linear batch mixing optimization programs can be utilized to predict which recycled components are the most limiting (economically and environmentally), thus preventing the need for time-consuming and expensive physical testing (such as x-ray diffraction or spectroscopy).

9.2.5 Identifying Undervalued Secondary Materials

- What collection, market, and manufacturing changes would need to occur to shift currently non-profitable recycled streams (e-waste, metallic dross, CRT glass) to a net positive?
- What drives secondary material availability and price?

Many material streams are currently being recycled due to regulations; unfortunately not because a commercially viable business market exists. One example includes electronic waste whose disposal is regulated due to the toxic heavy metals they contain. Another prime example is lead whose recycling rate is much higher than most materials (cf.) despite a lack of manufacturing sinks for recycled lead. Making these environmentally beneficial recyclers more economically viable would decrease the financial burden placed on other firms and tax-payers. Pinpointing the changes necessary for profitability to occur would be the first step in this direction.

9.2.6 Preventing "Down-cycling", Improved Recycling Operational Practices

- Are current operational strategies such as dilution and down-cycling economically and environmentally efficient?
- What untapped markets or higher value sinks exist for currently down-cycled secondary materials?

As discussed above, many recycled materials often include high levels of unwanted, or "tramp" elements that prevent their increased utilization. While upgrading strategies are one way to mitigate this, current practice relies heavily on dilution and down-cycling. Dilution is when secondary materials must be mixed with primary material to ensure the finished products meet compositional and performance specifications. While dilution is common; it has a negative impact on recycling as the required dilution results in a compositionally determined cap to recycling rates. "Down-cycling", where materials are recycled into lower value products, is another common method of dealing with highly contaminated secondary materials; this enables higher usage but negatively effects recycling economics. A specific example of down-cycling for the case of aluminum is when wrought scrap is used in cast products due to their ability to accommodate higher silicon contamination. To date, secondary aluminum production has focused on satisfying demand for compositionally forgiving cast alloys and the carefully designed alloy systems used for can stock. If secondary production is to sustain its current growth trend (which is far outpacing the growth in primary production(Kelly, Buckingham et al. 2004)), the sinks for secondary material will also need to expand. The economic and environmental impact of these operational strategies has not been explored previously.

9.2.7 Informing Recycling Systems Policy and Legislation

- How much should municipalities charge/pay for disposal of certain scraps?
- What are reasonable targets for recycling mandates created by legislators?
- Can one estimate recycling limits for products and/or materials systems in the US and globally?

Firms and legislators are often tasked with creating recycling targets. For example, Alcoa had a recent press release outlining goals of 25% recycled content in their fabricated product by 2010 and 50% by 2020. In 2000, the European Union set out legislation to require 95% of end-of-life vehicles be recycled by 2015(Union 2000). However, legislators in particular are often not equipped with the data and analytical tools necessary to make sure these targets are physical and economically possible. In fact, work done by Reuter, van Schaik, and others(van Schaik, Reuter et al. 2002; van Schaik and Reuter 2004; Reuter, van Schaik et al. 2006) has utilized dynamic modeling and extensive product data to examine optimal end-of-life vehicle recycling rates in the EU and concluded the 2015 directive an impossibility. This work demonstrates that detailed characterization of recycling systems is required to inform policy-makers in government and firms alike. One of the complexities in predicting recycling rates for recycling systems is the ever-changing nature of supply and demand. In light of the global trends, arguments could be made that nearly all materials are transitioning to exponential growth patterns. To determine the gross limits on recycling rates, it will be necessary to forecast this demand growth, evaluate scrap recovery rates, and determine product lifetimes and compositional deterioration.

Classically, materials design and technology decisions have been based on analysis of their desired properties such as strength, corrosion resistance, maximum operating temperature, etc. Adding environmental and economic implications to this analysis, however, is not straightforward as these are both context dependent properties as well as more difficult to quantify.

A variety of modeling tools are available to help support the decisions of secondary producers; many make use of linear optimization techniques (Lund, Tchobanoglous et al. 1994). These models can improve decisions about raw materials purchasing and mixing as well as the upgrading and sorting of secondary materials (Shih and Frey 1995; Stuart and Lu 2000; Cosquer and Kirchain 2003). Statistical analyses that are used to forecast expected outcomes may be used within such optimization tools to embed consideration of uncertainty in the decision-making. This can be quite powerful for certain types of analyses but deterministic approaches generally do not provide proactive mechanisms to modify production strategies as prevailing conditions evolve. Stochastic programming techniques can therefore be a powerful set of optimization tools that implicitly consider uncertainty. Recourse models(Gaustad, Li et al. 2006) and chance constrained programming(Gaustad, Das et al. 2007) are two types of stochastic models used in my dissertation to model recycling decision-making.

Additionally, simulation methods can be used to test the solution space of optimization problems. The Monte Carlo method uses pseudo-random numbers to statistically simulate random variables; this technique has been used successfully in my dissertation to model varying scrap composition for projecting error rates in secondary mixing strategies.

In regards to optimizing the architecture of recycling systems, a variety of models are available to examine the effectiveness of collection, disassembly, and processing steps(Johnson and Wang 1998; Kang and Schoenung 2006). Both network optimization models as well as reverse logistics can be utilized to examine the trade-offs of transportation, environmental benefit, and value. Life-cycle assessment is an extremely valuable modeling tool for characterizing the environmental impact of materials selection decisions. LCA methods make it possible to quantify the materials depletion, energy usage, emissions, and particulates of a particular product through-out its entire life-cycle including manufacturing, usage, and end-of-life. One can then map these quantities to a single impact assessment for comparison and evaluation.

Chapter 10. References

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Appendix. Additional data

A.1 Prices

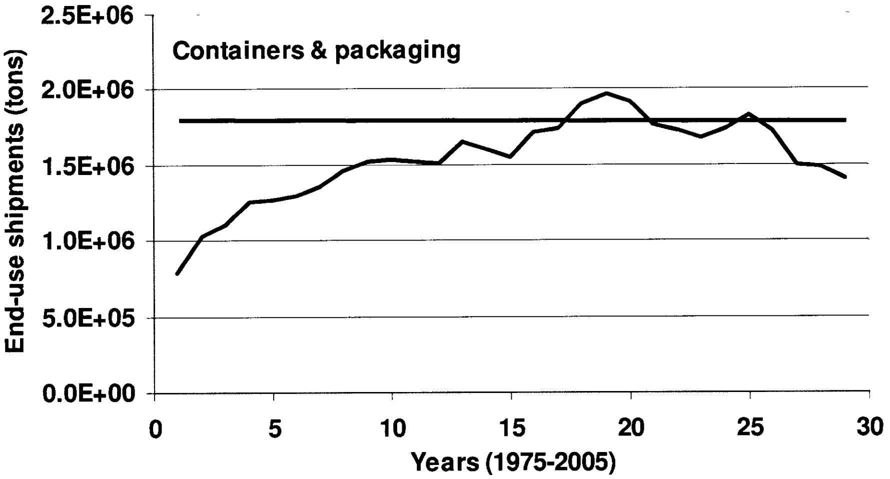
Prices of raw materials are extremely volatile as outlined in chapter 1; this is especially true of late due to the recent economic downturn. Because of this, the selection of prices to use for raw material feedstocks is challenging. The analysis in this thesis assumed the 2006 year average prices for primary aluminum and alloying elements as shown in Table XXXIX.

Table XXXIX. Average 2006 prices for raw materials from the USGS

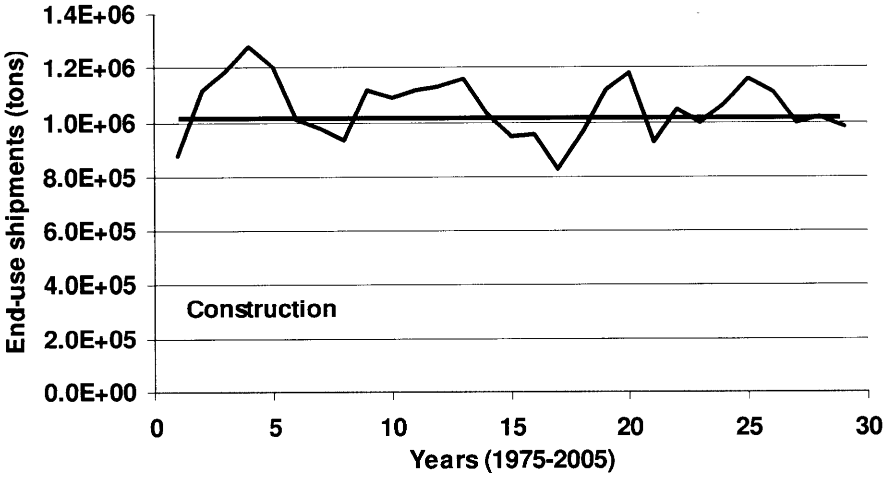
Raw Material	Average Price $/lb.
Primary Aluminum	$2.41
Silicon	$1.54
Manganese	$2.63
Iron	$0.44
Copper	$3.30
Zinc	$1.21
Magnesium	$2.70

A.2 Regression analysis of historical production

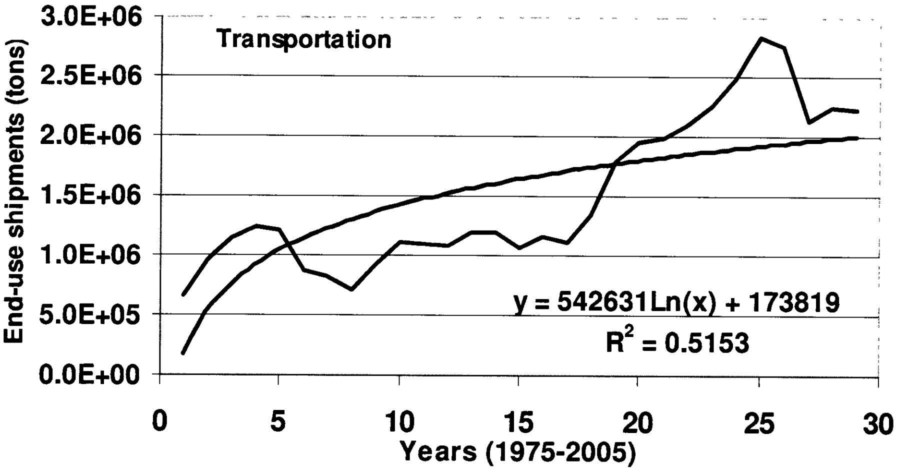
Table XXVII in chapter 6 summarizes the statistical regression analysis performed on the historical end-use shipments for the major aluminum product categories. The individual data and the subsequently selected trends for future projections are shown in A through H.



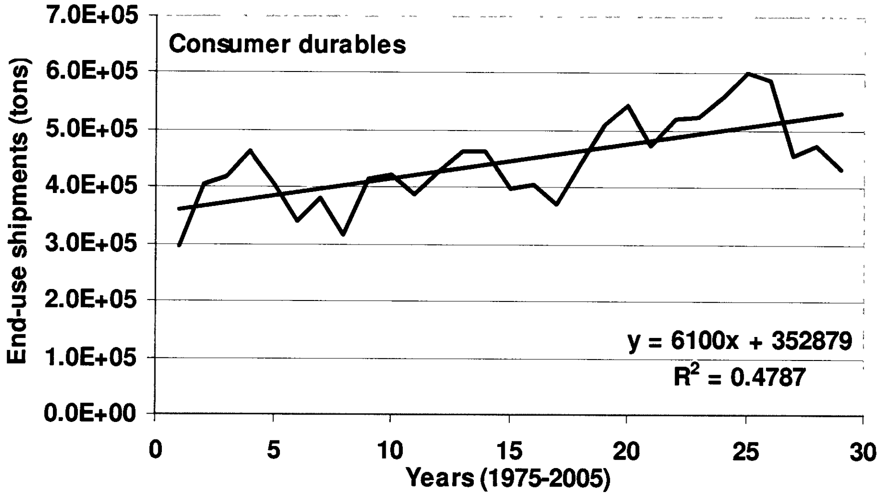
A)



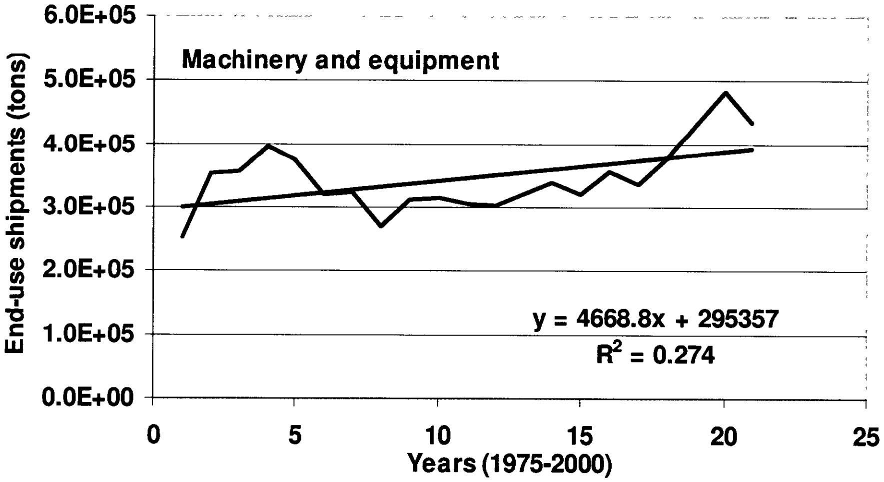
B)


Transportation
End-use shipments (tons)
3.0E+06
2.5E+06
2.0E+06
1.5E+06
1.0E+06
5.0E+05
0.0E+00
y = 542631Ln(x) + 173819
R² = 0.5153
0
5
10
15
20
25
30
Years (1975-2005)

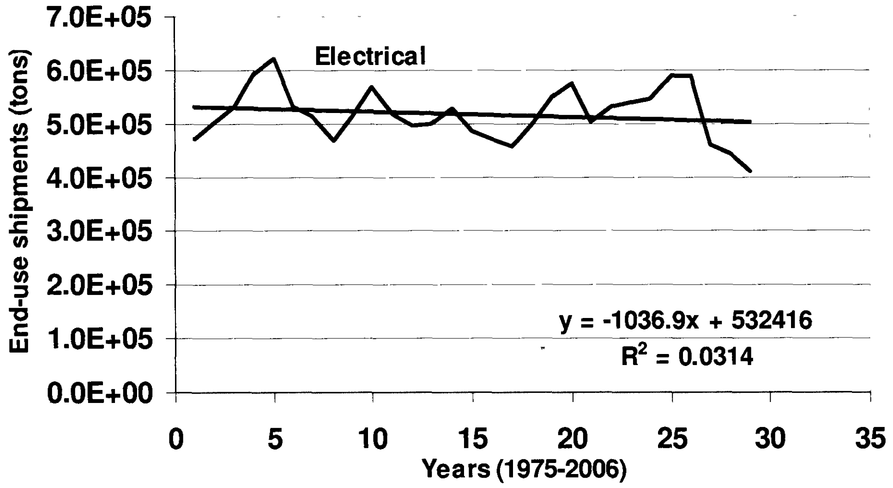
C)


Consumer durables
End-use shipments (tons)
7.0E+05
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0.0E+00
y = 6100x + 352879
R² = 0.4787
0
5
10
15
20
25
30
Years (1975-2005)

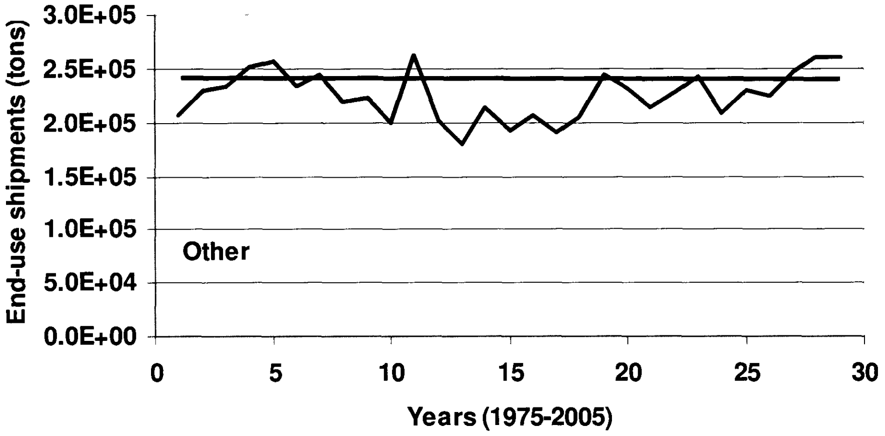
D)


Machinery and equipment
End-use shipments (tons)
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0.0E+00
y = 4668.8x + 295357
R² = 0.274
0
5
10
15
20
25
Years (1975-2000)

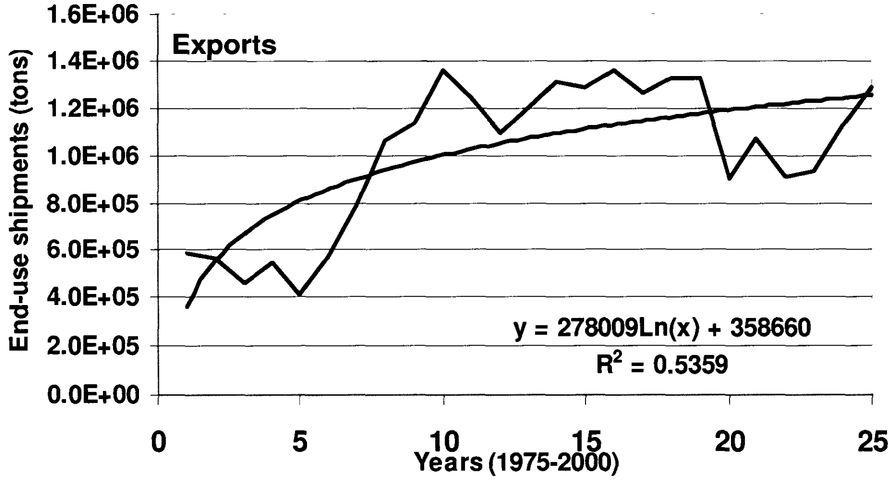
E)



F)



G)



H)

Figure 89. Individual product categories end-use shipments in the US with corresponding projection trend lines(Kelly and Matos 2006)