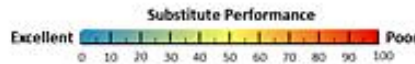


# Wastes as raw materials – and the central role of separation technologies

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Li 41	Be 63											B 41	C	N	O	F	Ne
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Rb	Sr 78	Y 95	Zr 66	Nb 42	Mo 70	Tc	Ru 63	Rh 98	Pd 39	Ag 44	Cd 38	In 60	Sn 36	Sb 57	Te 38	I	Xe
Cs	Ba 63	*	Hf 38	Ta 41	W 53	Re 70	Os 38	Ir 69	Pt 66	Au 40	Hg 45	Tl 100	Pb 100	Bi 46	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

* Lanthanides	La 75	Ce 60	Pr 41	Nd 41	Pm	Sm 38	Eu 100	Gd 63	Tb 63	Dy 100	Ho 63	Er 63	Tm 88	Yb 88	Lu 63
** Actinides	Ac	Th 35	Pa	U 63	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Graedel, Criticality of metals

David Allen  
 Department of Chemical Engineering  
 University of Texas at Austin

# How much Dysprosium to supply all of Texas electricity with wind?

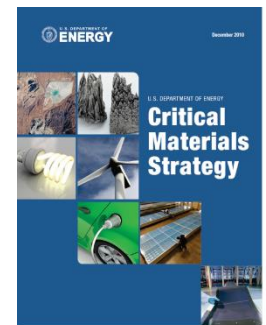
- 65 GW peak electricity production
- 20 – 30 kg MW
- 20,000-30,000 kg Dy per GW; 65 GW is 2 million kg, 2,000 tons
- World production is.....



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- Vehicles
- Lighting
- Solar PV
- Wind



# How much Dysprosium to supply all of Texas electricity with wind?

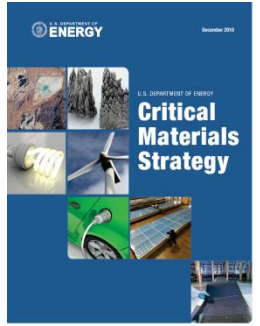
- 65 GW peak electricity production
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- 20,000-30,000 kg Dy per GW; 65 GW is 2 million kg, 2,000 tons
- World production is.....  
**<2000 tons/yr**



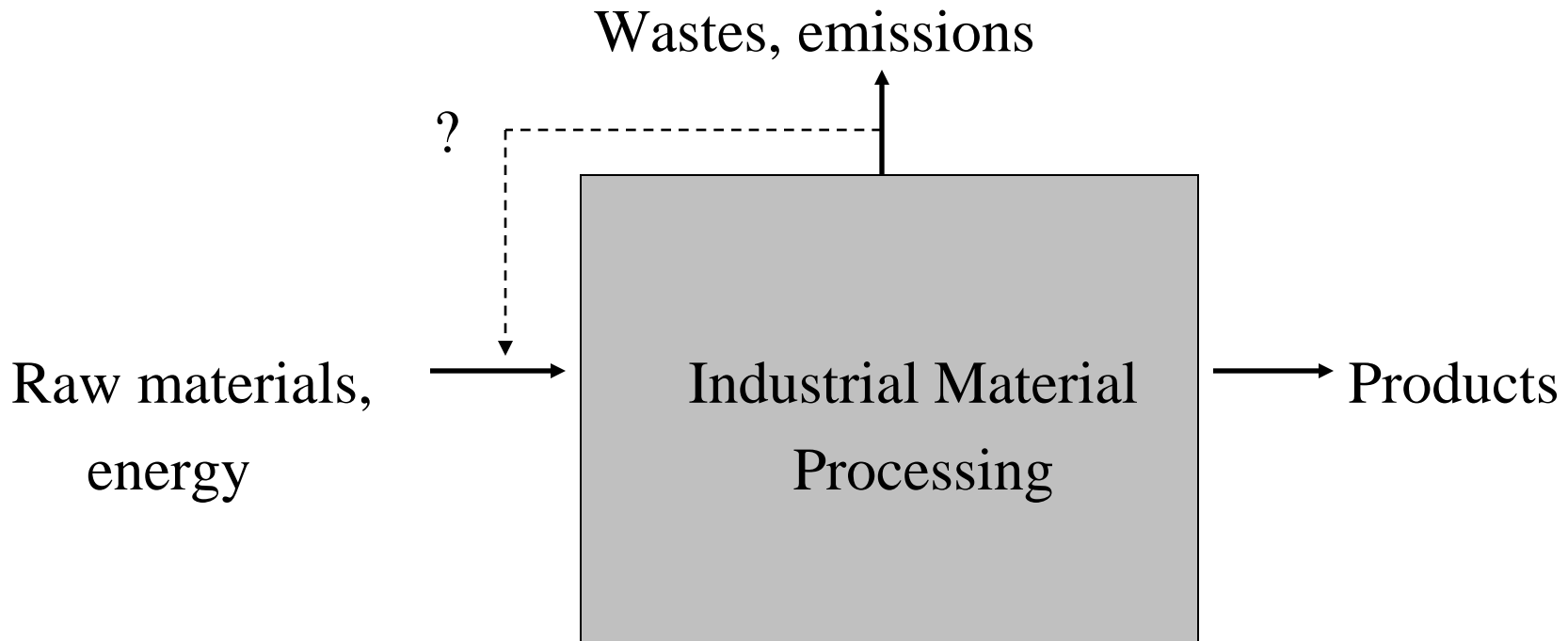
1																	2
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3	4											10					
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Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
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- Vehicles
- Lighting
- Solar PV
- Wind



For critical materials, can we design systems that use wastes as raw materials?



What can we learn from the history, over, the last several decades, of using wastes as raw materials?

# How much is out there?

Magnitudes of Waste Generation

# How much is out there?

## Magnitudes of Waste Generation

- 12 billion tons (wet basis) of industrial waste is generated annually in the United States
- Annual production of the top 50 commodity chemicals in the United States is 0.3 billion tons
- Annual output of U.S. refineries is 0.7 billion tons

To identify opportunities for using wastes as raw materials, we need data on waste streams

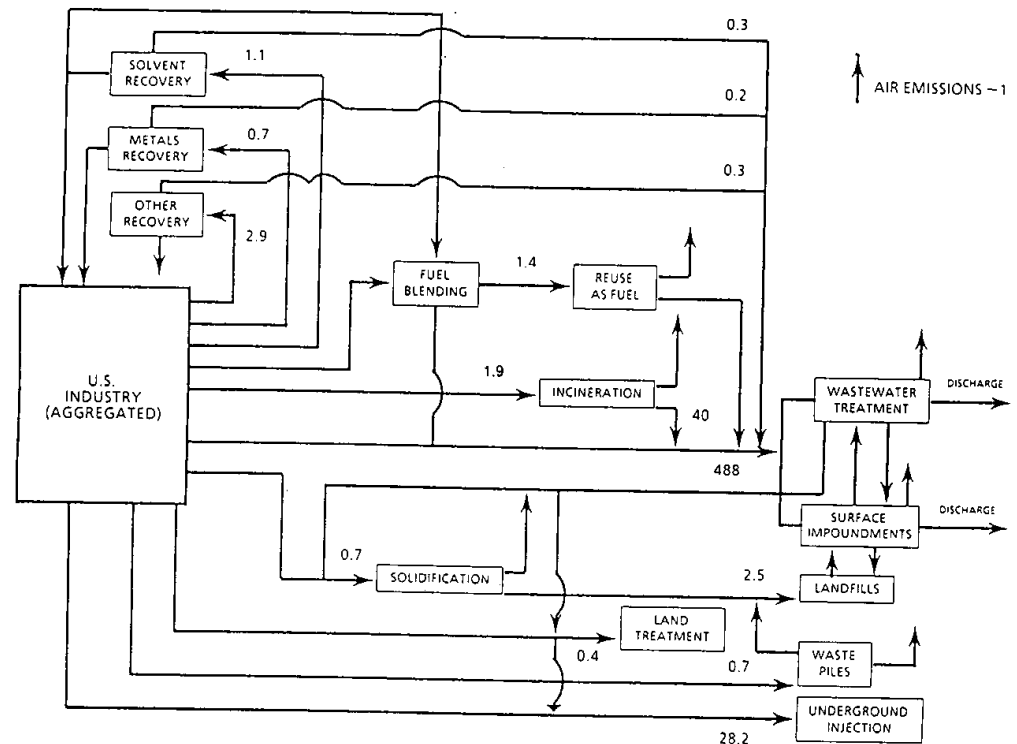
90-95% Industrial non-hazardous

5-7 % Industrial hazardous

2% Municipal solid

# Industrial Hazardous Waste

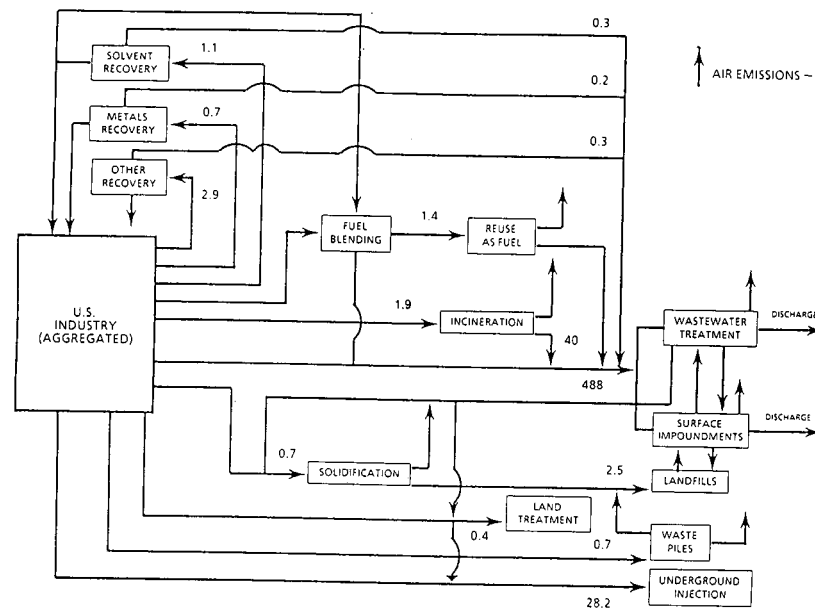
- 0.25 - 0.75 billion tons/year
- 75 - 90% from chemical manufacturing
- Much of the rest from petroleum refining





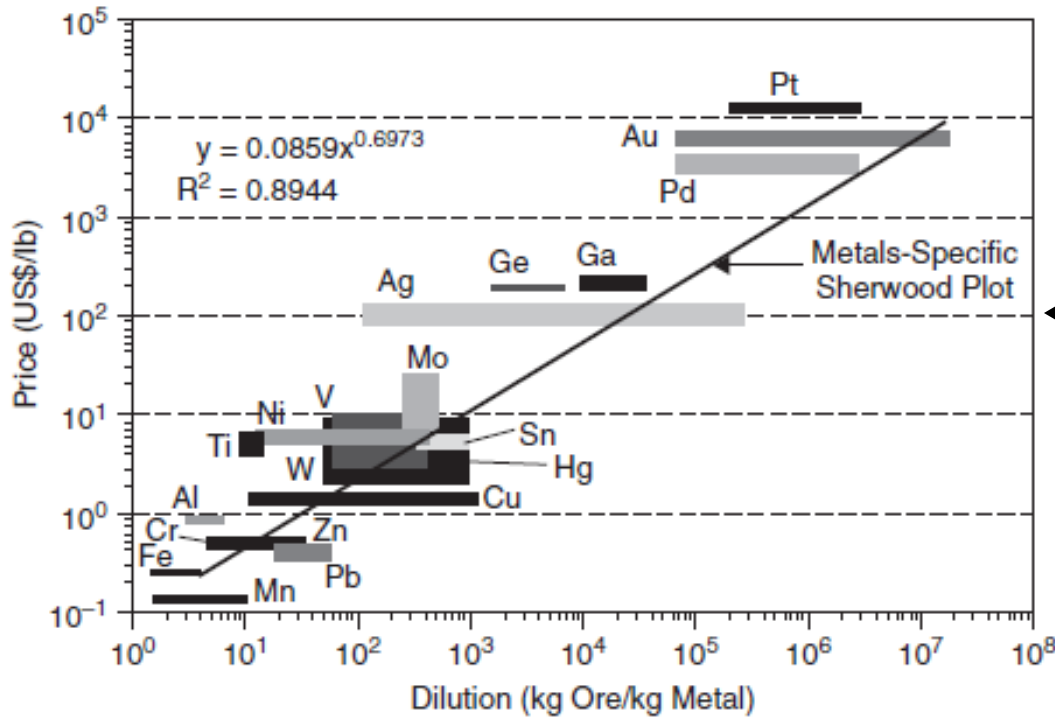
# Wastes as raw materials

## Flows of metals in hazardous wastes in the United States

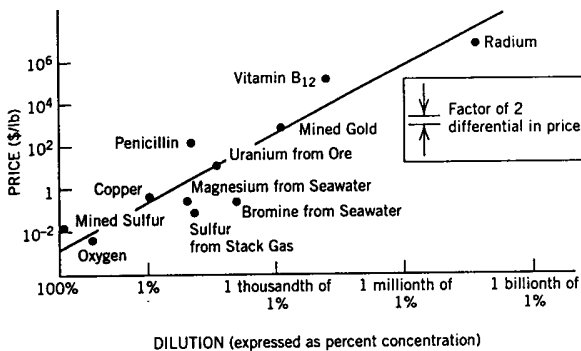


# Should we mine waste streams?

Consider the Sherwood diagram: value vs. dilution

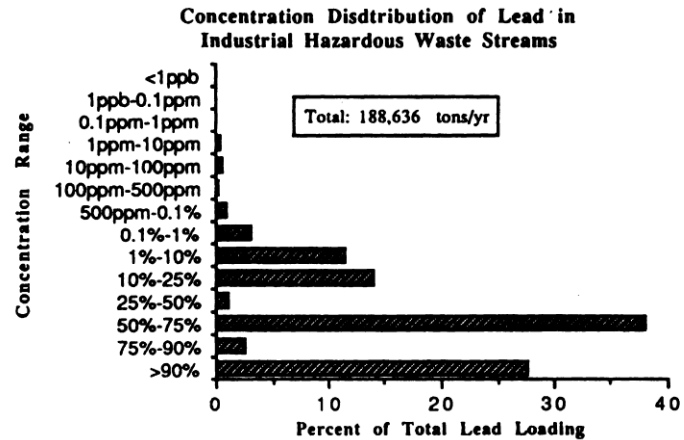
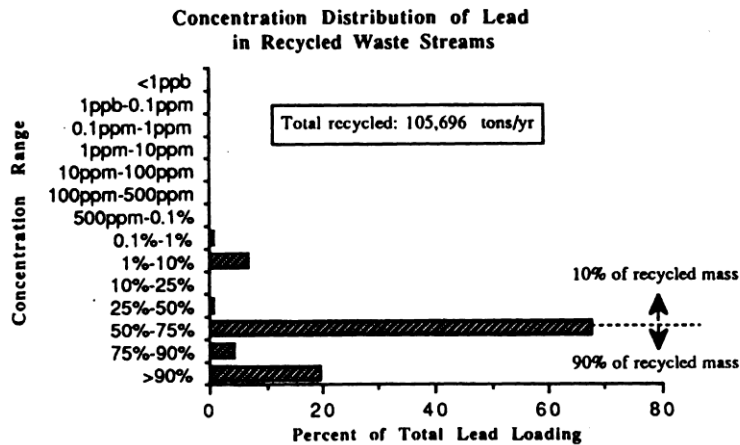


Very little of this cost is associated with the physical limits of overcoming the entropy of mixing



Update from Tom Graedel

# Many waste streams are surprisingly concentrated



# An economic opportunity?

Metal	Minimum Concentration Recoverable, from Sherwood Diagram (mass fraction)	Total Loading in Hazardous Waste Streams (tons/yr)	Recoverable Fraction of Metal in Waste	Percent of Metal Recycled from Waste Streams
Antimony	0.00405	17,000	0.74–0.87	35
Arsenic	0.00015	440	0.98–0.99	3
Barium	0.0015	59,000	0.95–0.98	1
Beryllium	0.012	5,300	0.54–0.84	11
Cadmium	0.0048	16,000	0.82–0.97	8
Chromium	0.0012	90,000	0.68–0.89	5
Copper	0.0022	110,000	0.85–0.92	10
Lead	0.074	190,000	0.84–0.95	56
Mercury	0.00012	5,400	0.99	16
Nickel	0.0066	3,600,000	1.00	0.1
Selenium	0.0002	2,000	0.93–0.95	29
Silver	0.000035	17,000	0.99–1.00	1
Thallium	0.00004	280	0.97–0.99	5
Vanadium	0.0002	4,400	0.74–0.98	1
Zinc	0.0012	270,000	0.95–0.98	12

Source: Data from Allen and Behmanesh (1993).

# If opportunities abound, why aren't they being exploited

Liability (user of the waste assumes legal liability)

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# If opportunities abound, why aren't they being exploited

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**Organization** (is using the waste part of the organization's core competency)

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**E**

**R**



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**Economies of Scale** (Is the material spatially distributed, and does this impose costs?)

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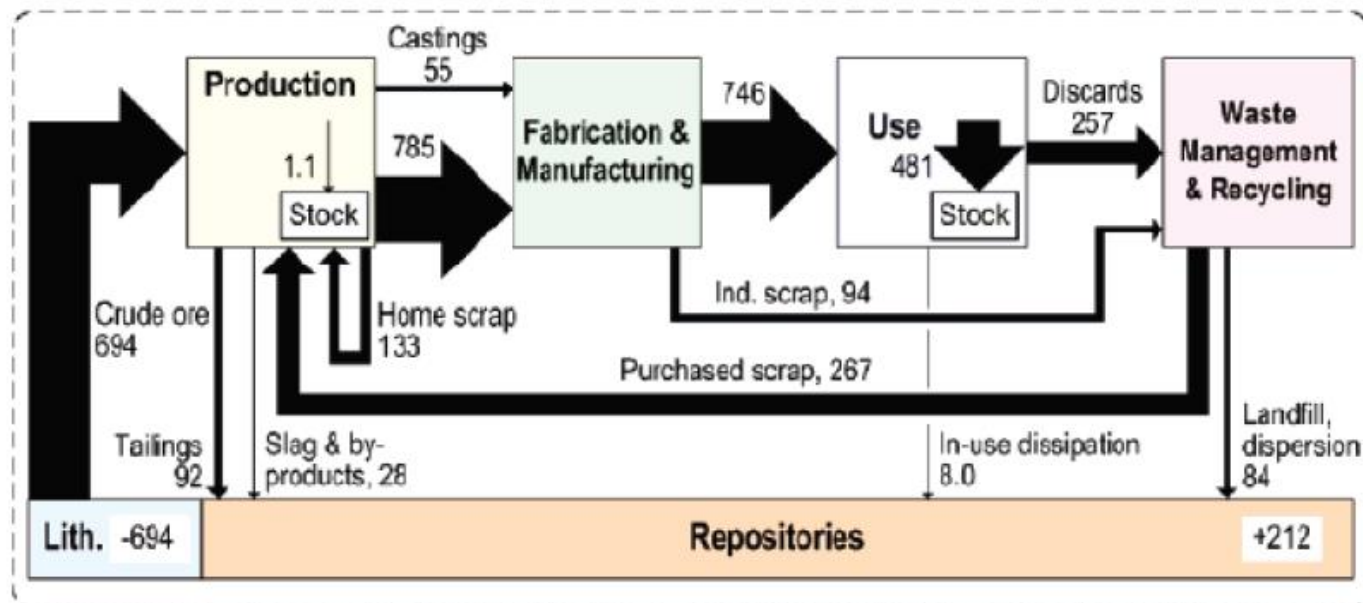
**Regulatory barriers**

Given these lessons from the recent history of using wastes as raw materials, what are key research needs?

Given these lessons from the recent history of using wastes as raw materials, what are key research needs?

Information,  
(separation) technology  
and economies of scale

# Information: where and what are the wastes and the material needs



Iron, 2000

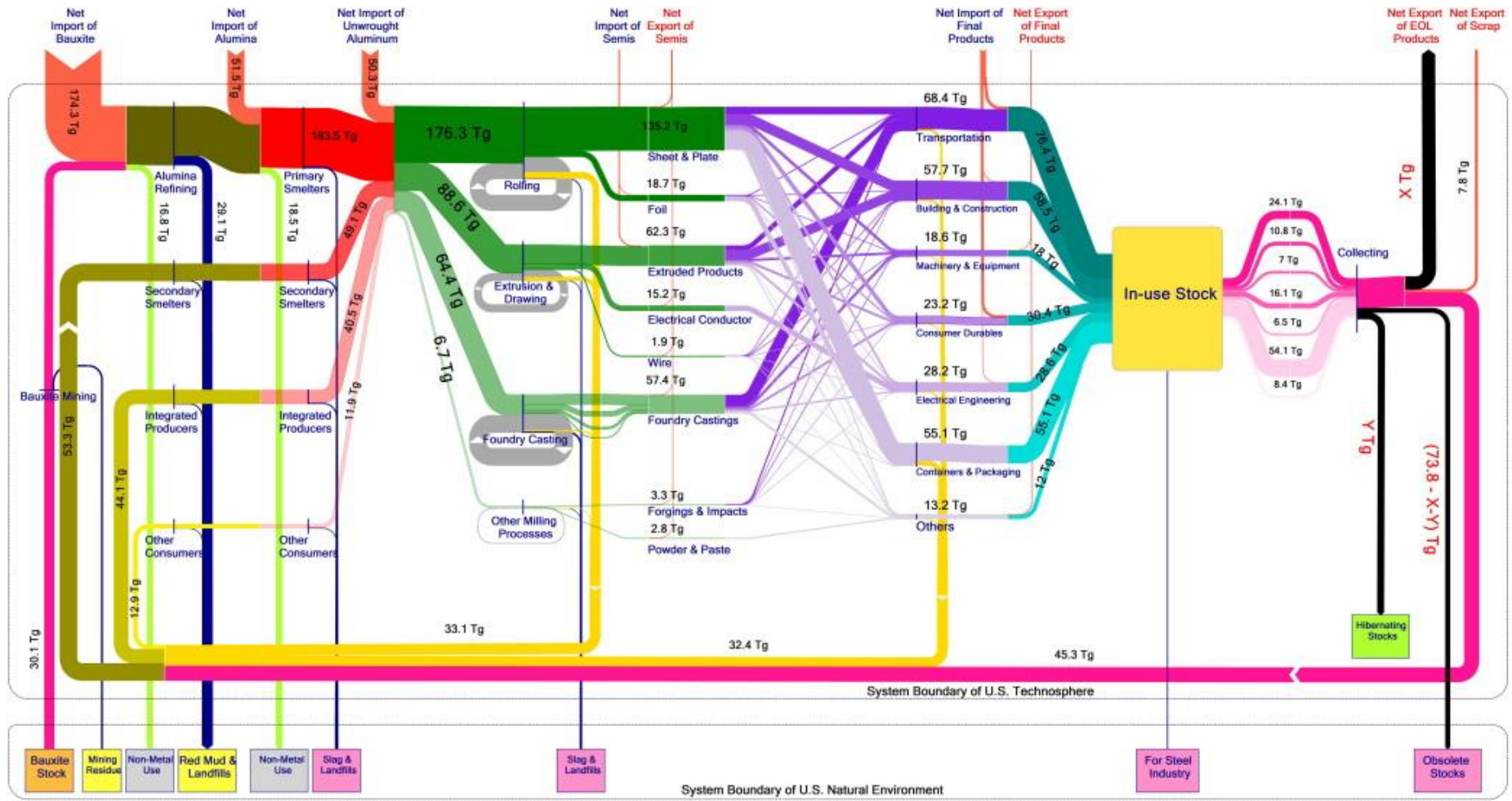
in Tg ( $10^9$  kg) Fe / annum

System Boundary: STAF World, Best Estimate

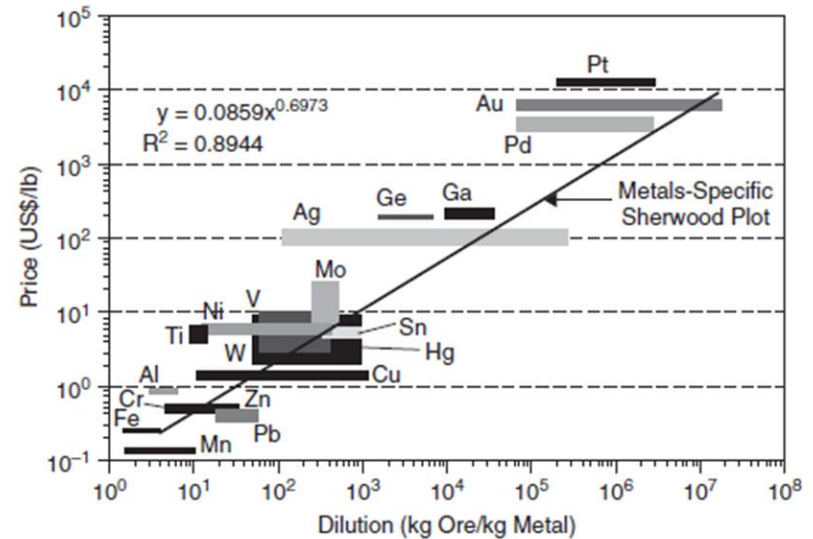
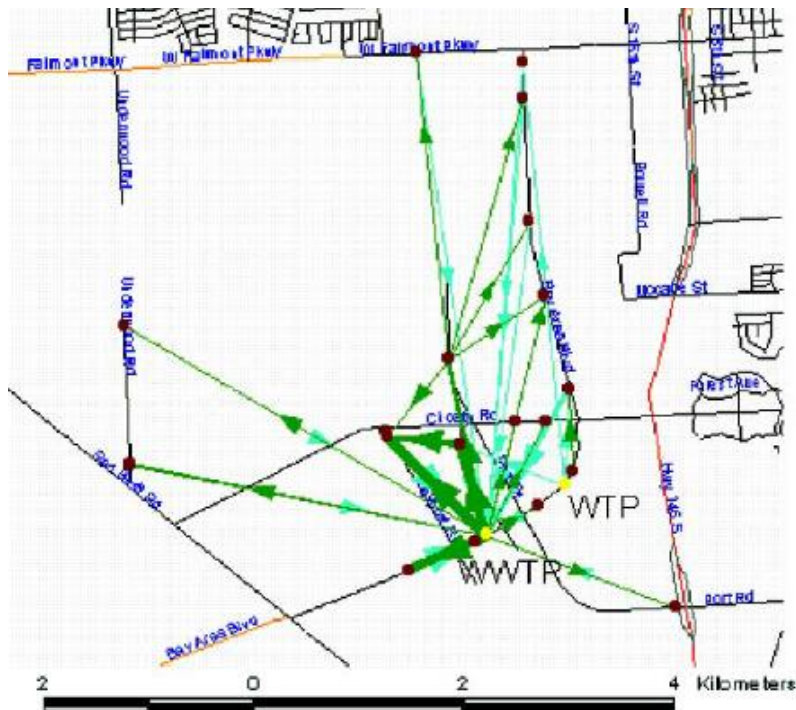
© 2006 STAF Project, Yale University



# Aluminum flows in the United States (Graedel)



# Economies of Scale: Need for detailed spatial mappings and concentration information



# (Separation) Technology

## Environmental Feasibility of the Recycling of Carbon Fibers from CFRPs by Solvolysis Using Supercritical Water

Marion Prinçaud,<sup>†</sup> Cyril Aymonier,<sup>‡</sup> Anne Loppinet-Serani,<sup>‡</sup> Nicolas Perry,<sup>§,8</sup> and Guido Sonnemann<sup>‡</sup>

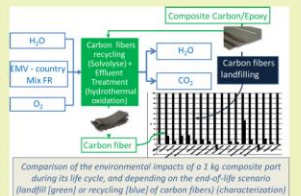
<sup>†</sup>Institut des Sciences Moléculaires Bât. A12, Univ. Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France

<sup>‡</sup>Institut de Chimie de la Matière Condensée de Bordeaux CNRS, Univ. Bordeaux, ICMCB, UPR 9048 87 avenue du Dr. Albert Schweitzer, 33608 Pessac Cedex, France

<sup>§</sup>Arts et Métiers ParisTech Bordeaux, I2M, UMR 5295, Univ. Bordeaux Esplanade des Arts et Métiers, 33405 Talence Cedex, France

**ABSTRACT:** Originally developed for high-tech applications in the aeronautic and aerospace industry, carbon/epoxy composites have been increasingly used in the automotive, leisure, and sports industries for several years. Nevertheless, the carbon reinforcement is an expensive constituent, and it has been recently shown that it is also the most environmentally impacting in a composite part manufacturing. Recycling these materials (even restricted to the reinforcement recovery) could lead to economic and environmental benefits, while satisfying legislative end-of-life requirements. The solvolysis of the matrix by water under supercritical conditions is an efficient solution to recover the carbon fiber reinforcement with mechanical properties closed to the ones of virgin fibers. This paper aims at demonstrating the environmental feasibility of the recycling of carbon fiber/thermoset matrix composites by solvolysis of the matrix in supercritical water. This demonstration is based on life cycle assessment that evaluates benefits and environmental challenges of this recycling loop.

**KEYWORDS:** Life cycle assessment (LCA), Supercritical water, Solvolysis, Recycling Composites, CFRP



### INTRODUCTION

Carbon fiber-reinforced plastics (CFRPs), or thermoset matrix composites, were originally developed for high-tech applications in the aeronautic and aerospace industry. For several years now, these materials have also been increasingly used in the automotive, leisure, and sports industries. In many applications in these sectors, one may seek aesthetic criterions or a simple feeling of high technology, more than highly technical properties. Thus, constituents' characteristics, and specifically reinforcements, are considered as a secondary matter and may be overemphasized regarding the function of the product. This is particularly true for nonstructural decorative parts (e.g., with a carbon look finish), for which the reinforcement is the most expensive constituent, and where glass fibers, much more less expensive, cannot be used.<sup>1,2</sup>

Today, there is no, or a limited, deposit (or very few) of carbon fibers from airplanes at the end of life because airplanes integrating such materials are only currently being built and will become waste later. In the future, the expected amount will grow year after year. Therefore, the question is this: Could carbon fibers recycled from airplanes (or from production waste from aircraft and automotive production) substitute mechanically for the majority of carbon fibers currently used in the automotive, leisure, and sports industries, considering that the recycling can be done in a cost-effective way and that the aeronautic industry will not use recycled fibers? Subsequent questions are these: How can carbon fiber-reinforced plastics be

recycled? Is the recycling environmentally more sustainable than the production of virgin carbon fibers?

One of the first uses of the supercritical fluid technology in the field of recycling was applied to polymers. This technique has been developed extensively in Japan since 1995 and has been reviewed many times.<sup>3–5</sup> Beyond plastics recycling, solvolysis in near- and supercritical fluids of thermosetting resins (phenol and epoxy resins) has attracted a great interest among the scientific community to recover materials like carbon fibers with a high added value in the past few years. To date, few studies have been carried out on the chemical recycling of these waste composites with near- and supercritical solvolysis technology.<sup>6–14</sup> Compared to other recycling processes (mechanical recycling processes, pyrolysis, fluidized bed processes, low temperature solvolysis processes), near- and supercritical solvolysis has the huge advantage that clean carbon fibers are recovered with similar mechanical properties to pristine fibers.<sup>6</sup> Moreover, these undamaged fibers are obtained at relatively low temperature, without using organic solvents or concentrated acids.

Near- and supercritical water and alcohols were mainly processed as solvolysis media. In fact, near- and supercritical water or alcohols play the role of solvent and reagent for the

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## Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling

Tom Vander Hoogerstraete, Sil Wellens, Katrien Verachtert and Koen Binnemans<sup>\*</sup>

An environmentally friendly process for the separation of the transition metals copper, cobalt, iron, manganese and zinc from rare earths by solvent extraction with the ionic liquid trihexyl(tetradecyl)phosphonium chloride has been developed. The solvent extraction process is carried out without the use of organic diluents or extra extraction agents and it can be applied as a sustainable hydrometallurgical method for removing transition metals from neodymium–iron–boron or samarium–cobalt permanent magnets. The recycling of rare earths is of high importance because of the possible supply risk of these elements in the near future. The method was tested for the removal of cobalt and iron from samarium and neodymium, respectively. The highest distribution ratios for cobalt and iron were found with 8.5 and 9 M HCl. At the tested conditions, the concentrations of neodymium and samarium in the ionic liquid were below 0.5 mg L<sup>-1</sup> (0.5 ppm), even for feed concentrations of 45 g L<sup>-1</sup>. The separation factors of Nd/Fe and Sm/Co are 5.0 × 10<sup>6</sup> and 8.0 × 10<sup>5</sup>, respectively. The percentage extraction of iron is still higher than 99.98% at loadings of the ionic liquids with 70 g L<sup>-1</sup> of iron. The viscosity of the ionic liquid containing the tetrachloroferrate(II) complex [FeCl<sub>4</sub>]<sup>2-</sup> is lower, and less depending on the feed concentration, than in the case with a tetrachlorocobaltate(II) anion [CoCl<sub>4</sub>]<sup>2-</sup>. After extraction, cobalt can be stripped very easily from the ionic liquid phase with water. However, due to the very high distribution ratio, iron could only be stripped by forming a water-soluble iron complex with ethylenediaminetetraacetic acid (EDTA). Also the possibility to extract chromium, nickel, aluminium, calcium and magnesium with trihexyl(tetradecyl)phosphonium chloride has been investigated, but the distribution ratios of these elements are very low in the tested conditions.

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www.rsc.org/greenchem

### Introduction

Liquid–liquid extraction (solvent extraction) is the most commonly applied technique for the separation of metal ions. In this technique, the aqueous phase containing a metal salt is mixed with an organic phase containing an extraction agent (extractant).<sup>1–3</sup> The metal ion forms a hydrophobic complex with the extraction agent and migrates to the organic phase. The separation of metals is based on differences in the affinity of complexes for different metals in the organic phase, as well as on the relative solubilities of the complexes in the aqueous and organic phase. The simplicity with which the parameters controlling extraction, such as the organic phase, pH or extractant, can be changed is a major advantage of solvent

extraction. The water-immiscible organic phase often consists of a volatile and flammable solvent, such as kerosene, toluene, dichloromethane or diethyl ether. Ionic liquids (ILs) are greener and safer alternatives for these molecular solvents,<sup>4–7</sup> and have already successfully been applied for the extraction of metal ions.<sup>8–17</sup> Ionic liquid solvents are organic salts which consist entirely of ions and typically have a melting point below 100 °C.<sup>18–20</sup> Their negligible vapour pressure and non-flammability make this class of solvents safer and more environmentally friendly than molecular solvents that are commonly applied in biphasic extraction systems.<sup>21</sup> In many cases, metal extractions with ionic liquids occur via an ion-exchange process,<sup>22–25</sup> in which a neutral extractant (e.g. crown ether, amine) transfers the positively charged metal ion to the ionic liquid phase. In order to obtain charge neutrality, the cation of the ionic liquid has to dissolve into the aqueous phase where it forms a new ionic liquid with the anions of the metal. This loss of ionic liquid can be alleviated by introducing long alkyl chains on the cation or by using fluorinated anions such as

KU Leuven – University of Leuven, Department of Chemistry, Celestijnenlaan 200F, bus 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@chem.kuleuven.be; Fax: +32 16 32 79 92



# If opportunities abound, why aren't they being exploited

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(separation) technology  
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