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ENERGY EFFICIENT MATERIALS MANUFACTURING FROM SECONDARY RESOURCES

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Abstract

Rare earths metals, including yttrium and scandium, are being increasingly used in clean energy technologies, colored phosphors, lasers and high intensity magnets. There are important defense applications such as fighter jet engines, missile guidance systems and space based satellite and communication systems, based on these metals. The commitment to clean energy technologies by various governments, as well as the projected growth in power and transportation sectors across the globe will certainly escalate the demand for rare earth metals and compounds. This demand implies that to ensure unhindered technological innovation, it is essential to possess secure supply chains for rare earth elements. The United States continues to be one of the largest consumers and importer of rare earths and the trend is expected to continue as the demand increases. In order to ensure secure rare earth supply and attenuate supply-demand imbalances post 2014, it is not only necessary to encourage and support exploration of newer reserves, build a rare earth stockpile, but it is also of utmost importance to look at opportunities to recycle and reuse Rare Earth Elements (REE) from secondary sources, such as post-consumer and manufacturing process wastes. This research describes the technological developments made to convert these valuable resources into functional manufactured materials for lighting industry, automotive and petroleum refining catalysts, and high density permanent magnets. In addition, production of rhenium from advanced aerospace alloys is also discussed from the perspective that it can be recovered for introduction in turbine alloys.

CONTEXT

Sustainable development in the 21st century is perhaps the most pressing issue we face. At the same time, it is also a time for remarkable opportunities for materials scientists and engineers (MSE) as many of the solution pathways to these challenges are materials centric.

To put things in context, it is important for us to understand the magnitude of the issues we face. Since 1700's the volume of goods traded Increased 800 fold. Between 1910-2010 the

World's industrial production Increased 100+ fold. And between 1900-2000 global consumption of fossil fuel Increased by 50 fold. These are highlighted below.

- World population is estimated to rise to over 9 billion in the next 3-4 decades. Between the period 1960-1975, a billion people were added, and another billion between the period 1975-1987. Keep in mind that we entered the 20th century with only 1.6 billion people, and exited the same century with 6.1 billion! Furthermore, the population growth is not evenly distributed throughout the world; the growth is occurring more in less developed countries.

- More people equates to more consumption and more energy usage. Our "hunger" for energy is huge. Though population is growing at an average of 1.4% a year, our need for energy is growing at an average rate of 1.7%; certainly not a tenable scenario. Average energy consumption per capita throughout the world is about 57 gigajoules, and for USA it is 230 gigajoules, and 119 for Europe. Such consumption of energy is not sustainable.

- Associated with energy usage is the production of greenhouse gases, which have adverse effects on our climate and the environment. There are many debates on the assumptions used in the various models that predict global warming and the levels of CO2 production. One thing that is not debatable is that we need to reduce generation of greenhouse gases.

- Food and water, basic human needs is also being taxed. 18% of the world population lacks access to safe drinking water. 20% of the world population is living in absolute poverty (defined as living on less than one Dollar per day); about 1.4 billion people! To exacerbate the situation, 40% of the world population has no access to sanitation.

- Urbanization is a phenomenon that has major ramifications. Sustainable mobility – transportation needs- is a significant issue for two reasons. The infrastructure that was built for a world of 5 billion cannot sustain 7 billion plus people. We have major infrastructural gaps. The other reason is that transportation systems are lacking, except in a few countries and major cities, which have become a benchmark for the rest.

- Housing and shelter needs of the world are also increasing, and on the human side, the need for community which is so vital for a quality life.

- Material consumption is at all time high. Many consumer goods are packaged, and the amount of waste that is created per capita is growing. If one considers the amount of material that is recovered and recycled in the overall system, it is pitiful. The average per capita consumption is about 50Kg per person. In the US, only about 50% of beverage cans are recycled, and only ~30% of glass bottles. More recently, if we look at the price of rare earths, we can see the dramatic increases in price. Inorganic materials are not renewable, and they need to be recovered and recycled.

- Lastly, health is perhaps the most critical human need, and life expectancy around the world has increased significantly (in US alone it has gone from 70 yrs in the mid 1950's to close to 80 years old at present), with the exception being Africa. Health care needs around the world have increased, and the cost of health care delivery has also skyrocketed.

PRESENT SCENARIO

Increasingly, the U.S. government, academia, domestic industry, and the public acknowledge the imperative that we need to conserve energy and natural resources while exercising judicious stewardship of the environment. The issue of sustainability is and should be paramount in how we design, manufacture, use, and retire the many products we consume throughout the world. Inorganic materials are not renewable; the need exists for the development of technologies to address materials recovery and recycling. Research supporting materials recovery and recyclability is inherently multidisciplinary and must respond to the needs of a multiplicity of commercial stakeholders from throughout the materials supply chain.

Despite growing efforts to recycle metals, we fail to recover half of the domestic post-consumer metal scrap reclaimable from retired products, and we continue to rely on primary metals production to fulfill two thirds of our manufacturing needs. Use of primary metals, in lieu of scrap, increases global energy consumption as well as the production of greenhouse gases. In order to augment recycling rates the materials community needs to upgrade recovery and recycling processing technologies to maximize the capture of post-consumer scrap and minimize the quantity of manufacturing scrap.

Rare earth elements are a group of 17 elements, which include 15 Lanthanides, Scandium and Yttrium. In spite of what the name suggests these elements are not “rare”. However, in recent years rare earth elements have become strategically critical for developed and developing economies around the world which is primarily due to the shortage of discovered minable resources [1]. Before 1948, the placer deposits of Brazil and India were the chief sources of rare earth metals for the rest of the world. With increasing demand newer supply sources were needed and for a while the monazite deposits in South Africa played an important role before the production was dominated by Bastnasite reserves in Mountain Pass and China [2].

According to a forecast done by IMCOA, the world rare earth demand is projected to rise to 200,000 tons by 2014 and the Chinese production is expected to be around 160,000 tons [3]. In addition, the demand of rare earths in China itself has increased by 380% between 2000 and 2009, which is believed to be the primary reason behind the export cuts on rare earth [4]. These developments have made rare earth elements a strategically important material as evident by the Rare Earths and Critical Material Revitalization Act of 2010 approved on September 29, 2010 which aims to establish an R&D program within the DOE to assure long term supply of rare earth materials [5]. The US Department of Energy published an analysis of the criticality of selected rare metals, the most critical elements were identified to be Dysprosium, Neodymium, Terbium, Yttrium and Europium - what are also known as the heavy rare earth elements [6]. Based on the demand and supply position of common rare-earths, the prices of common metals like Ce, Nd, Sm, La and Y, went up by 150% to 700% in a short period of six months between January and August 2010 (Table 1).

Table 1: Price Variation of Prominent Rare-earth Metals

REE	Price $/kg *Jan. 2010*	Price $/kg *Aug., 2010*	% Increase
Yttrium	10.25	34.50	**236%**
Neodymium	22.50	55.25	**146%**
Lanthanum	5.60	33.50	**498%**
Samarium	3.95	31.80	**705%**
Cerium	4.15	33.00	**695%**

According to a survey conducted by IMCOA in 2008 and reported by Kingsnorth, the chief users of rare earth metal by weight, are catalysts (68%), ceramics (7%), metal alloys (7%), polishing (5%), glass (5%), magnets (4%) and phosphors (3%). By 2014 it is projected that the major users of rare earth metals by weight would be metal alloys (25%), magnets (23%), catalysts (16%), polishing (11%), phosphors (7%) and glass (7%). These applications of rare earth metals provide opportunities for recycling through strategic end of life management. Many of the applications could provide efficient sources for heavy rare earth elements which are scarce and, at the same time, critical for development of new technologies. For example, recycling of compact and linear fluorescent lamps can prove to be a useful source of Yttrium, Europium and Terbium whereas recycling of permanent RE magnets used in wind and hydro power generation can become an important secondary source of Neodymium, Praseodymium, Dysprosium and Terbium. The elemental content of rare earths in appropriately sized phosphor dust that is generated from spent lamps exceeds fifteen percent.

Till now, recycling of rare earth has not been implemented on a large industrial scale. Ellis, Schmidt and Jones [7] have reported that recycling of rare earth based materials would have a stabilizing effect on price, supply, and quality. In addition, an infrastructure does not exist for the recycling of rare earth based materials. Higher volume application of rare earth based materials seems eminent, and therefore, the time is right to develop both the technology and infrastructure. Researchers have shown that aqueous processes, as well as molten slag electrorefining techniques are viable methods for returning high purity metals, but have limitations in their ability to be selective and cannot handle all kinds of wastes, such as swarf. Liquid-liquid extraction using metallic solvents presents interesting opportunities that overcome the shortcomings of the other methods. However, more research is required to develop technologies for commercial use [7].

Several constraints on recycling of rare earth were reported in an analysis by Okie-Institute AV [8], such as - need for an efficient collection system, need for sufficiently high prices for primary and secondary rare earth compounds, losses of post-consumer goods by exports to developing countries and the long life time of products such as electric motors and wind turbines. Zhong et. al. suggested that 20-30 % REE magnets are scrapped during manufacturing stage [9]. Other researchers have suggested various pyrometallurgical and hydrometallurgical routes to recover REE from these scrapped magnets [10]. Efforts have also been made to recover REE from used Ni-MH batteries. During pyrometallurgical treatment of these batteries the REEs report to the slag. Various hydrometallurgical routes have been investigated to recover these elements [11,12,13]. Recycling of rare earths from phosphors, as discussed above, provides an efficient way to recover high value heavy rare earth elements. Mei et. al. has provided an overview of various possible recycling methods for recovery of rare earths from fluorescent powder [14]. Not much work has been done on recycling of rare earths from catalysts. Catalysts primarily contain low value light rare earths like lanthanum and cerium which might be one of the reasons why not much effort has been put in this direction. However, once the economics of recycling of REE from spent catalysts becomes favorable, one would expect to recover the light rare earths feasibly and return them back to manufacturing.

A number of extraction processes have been successfully evaluated for application but not many have been commercially developed. However, the impending problem of supply shortage and the soaring prices of rare earths have made the environment conducive to build a recycling economy of these metals to address the problems. Such a strategy, if successfully implemented, would encourage research and development of green technologies and other critical areas by minimizing dependence on unpredictable nature of Chinese rare earth supply. This change in supply scenario, of course, will depend on the specific type of metal and material and its demand. In addition, some of the ‘exotic’ metals, such as rare-earths, molybdenum, rhenium, ruthenium, tungsten, PGMs, etc, for which demand is predicted to stay high and the indigenous resources low, recycling and recovery from spent secondary resources will be only viable option for sustainable growth.

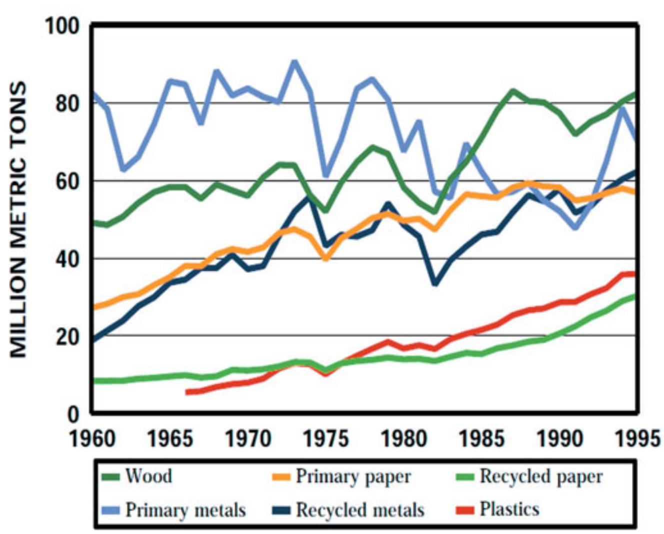

Fig 1: The Consumption of Primary Metals in the US indicates a steady trend from 1960-95, but the recycled metals consumption shows a growth of over 200 percent. (Matos & Wagner, 1996) [15].

Recycling of metals in the US has shown a growing trend over the past five decades (Fig.1). Recycling provides energy conservation, better environmental control and improved economic process viability for most metals and materials. Many industrially significant metals do indicate higher demand than supply and must find ways to recover these from spent sources, as shown in Table 2. Terbium, dysprosium and yttrium are used in fluorescent light fixtures while neodymium and samarium are used in permanent magnet production.

Table 2: Yttrium, Terbium and Dysprosium show a shortfall in supply compared with other rare-earth metals.

Rare Earth Oxide	Demand REO Tonnes	%	Supply/Production REO Tonnes	%
Lanthanum	51,050	28.4%	54,750	26.9%
Cerium	65,750	36.5%	81,750	40.2%
Praseodymium	7,900	4.4%	10,000	4.9%
Neodymium	34,900	19.4%	33,000	16.3%
Samarium	1,390	0.8%	4,000	2.0%
Europium	840	0.5%	850	0.4%
Gadolinium	2,300	1.3%	3,000	1.5%
Terbium	590	0.3%	350	0.2%
Dysprosium	2,040	1.1%	1,750	0.9%
Erbium	940	0.5%	1,000	0.5%
Yttrium	12,100	6.7%	11,750	5.7%
Ho-Tm-Yb-Lu	200	0.1%	1,300	0.5%
Total	**180,000**	**100%**	**203,500**	**100.0%**

TECHNOLOGICAL OPTIONS

Comprehensive reports are available that detail the technological options for rare earth metals recovery from spent phosphor dust [8]. A US patent is also found on the process [16]. A major initiative for resource recovery and recycling was initiated by funding from the National Science Foundation in USA. The Center for Resource Recovery and Recycling (CR^3) is a multi-university Center with WPI, CSM and KU Leuven. See www.wpi.edu/+mpi. Within the Center a major portion of the research portfolio is devoted to the recovery of valuable elements. One project is devoted to the recovery of REE from magnets, another from phosphors, and bauxite etc. The matrix given below - Figure 2 - can best describe the research portfolio of CR^3.

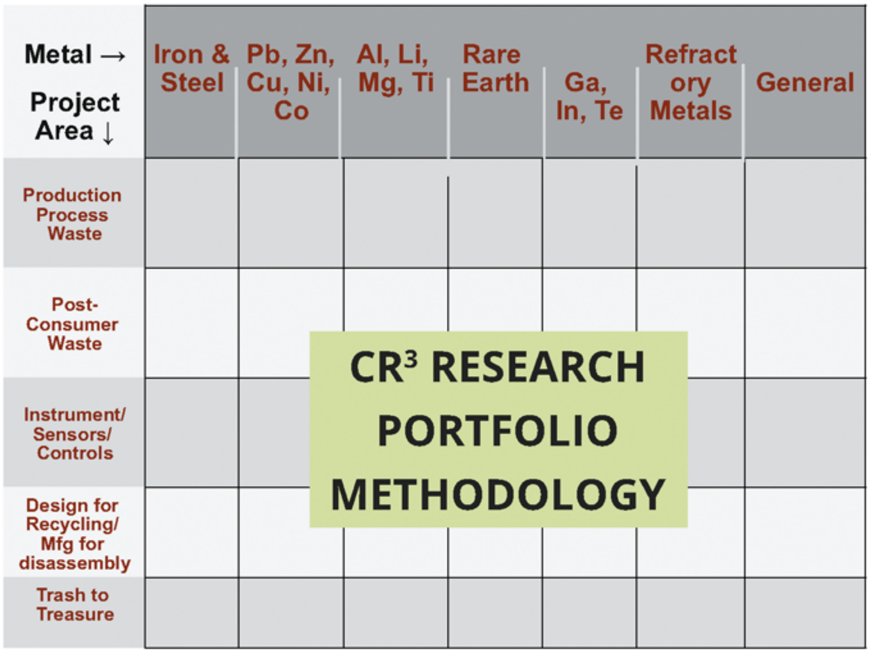

Fig 2: Matrix describing the research portfolio of the Center for Resource Recovery and Recycling (CR^3).

The research group at CSM using the process flow-sheet given below has developed the recovery of rare-earth metals from the spent phosphor dust - see Figure 3. This flow sheet allows the recovery of Eu & Y separately from La, Ce and Tb with over 90% recovery of each of the metals. The RE metal oxide mixtures are over 99% pure. The first step separates most of the glass from the phosphor dust. The easily soluble oxides of Eu and Y are taken into solution and precipitated out as an oxalate. The residue is roasted at high temperature to break down the phosphates, which allows the dissolution and recovery of the difficult RE oxides of La, Ce and Tb. The optimized process includes two pyrometallurgical steps following the two acid digestion and precipitation steps, and results in the recovery of all the five RE metals contained.

The advances made in recovering an ‘exotic’ metal such as rhenium, is described here, which will allow its return to the manufacture of superalloys. Driven by the superalloy sector, which accounts for 80 percent use of Rhenium metal, an annual growth in demand of an average of 5 percent is predicted over the next five years. The current global production is estimated at 50 mT. This demand growth is triggered by an expansion in primary production capacity, greater recycling of rhenium-bearing superalloy scrap and increased use of superalloy ‘revert’. Rhenium is used as an additive to tungsten and molybdenum-based alloys, filaments for mass spectrographs and ion gauges, Rhenium-molybdenum alloys in super-conductors at 10K, electrical contact material due to high wear and arc-corrosion resistance and thermocouples of Re-W for high temperatures. In addition to being produced as a byproduct of molybdenum, it is possible to recycle rhenium during processing and after its use.

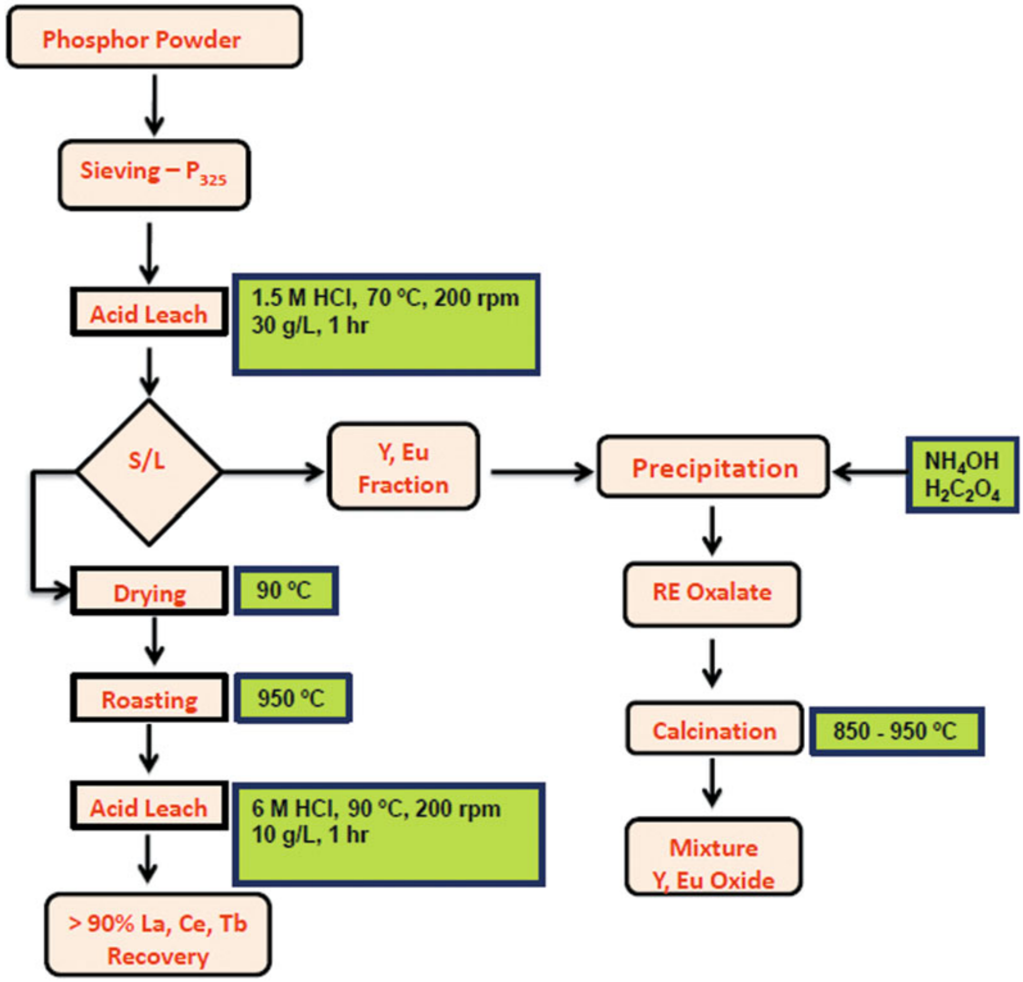

Fig 3: Flow sheet for the recovery of rare-earth metals from spent phosphor dust.

Recovery and Refining of Rhenium, Tungsten, and Molybdenum from W-Re, Mo-Re, and other Superalloy Scraps have been carried out via an oxidative pyrometallurgical roast technique. Initially, the scrap is roasted at 1000°C under an oxidizing atmosphere to convert the contained rhenium to water-soluble rhenium pentoxide (Re_2O_7). The volatile rhenium pentoxide is condensed in the cooler part of the tube furnace. This condensed material is then sent for digestion in water. The aqueous rhenium (ReO_4^-) is subsequently precipitated as potassium perrhenate upon the addition of potassium chloride via the following reaction:

$$KCl + ReO_4^- = KReO_4 + Cl^- \qquad (1)$$

The potassium perrhenate is filtered and further purified via continued dissolution and recrystallization. After purification, the salt is dried and sent for reduction under a hydrogen atmosphere at approximately 350°C via the following reaction.

$$2KReO_{4(s)} + 7H_{2(g)} = 2Re^o + 2KOH_{(s)} + 6H_2O_{(g)} \qquad (2)$$

The metallic rhenium is first washed with distilled water, and then 95% ethanol to remove any residual alkali salts. (Heshmatpour, 1982)[17].

The process of Rhenium Recovery from Spent Platinum Rhenium Catalyst relies on the use of sulfuric acid for the dissolution of alumina, rhenium, and to some extent platinum. The rhenium rich solution is separated from the platinum-containing residue and separated from the aqueous aluminum using ion exchange. Rhenium is subsequently eluted from the organic amine resin by way of hydrochloric acid addition. After elution, the rhenium rich eluate is neutralized using ammonium hydroxide. This solution is then evaporated to form a super-saturated solution, and cooled to allow for crystallization of ammonium perrhenate. After continued re-dissolution and recrystallization, a high purity ammonium perrhenate precipitate is obtained (El Guindy, 1997)[18].

A process for the electrolytic decomposition of rhenium superalloys has shown favorable results (US Patent # 0110767). The developers describe a process where titanium baskets, which act as the electrodes, containing superalloy scrap are fed to a polypropylene electrolysis cell containing an 18% HCl solution. The electrolytic dissolution is carried out for 25 hours at a frequency of 0.5Hz, current of 50 amps, voltage of 3-4V, and a temperature of 70°C. The remaining scrap is then filtered from the pregnant solution and sent for further dissolution in sodium hydroxide/peroxide solution. These processes that have shown technical viability on a lab-scale have to be further optimized for commercialization.

SUMMARY

Recycling of these critical and other strategic metals will become a necessity, as demand will outstrip the supply in the future, particularly in US due to import fluctuations. Controlled and reliable source for spent secondary resources will be required. Technologies will have to be developed that are optimized not only economically but also energetically and environmentally. Better separation and scrap-sortation schemes have to be adopted followed by adequate beneficiation and chemical/metallurgical recovery processes. Just as steel and aluminum, these strategic metals primary production will have to be supplemented by secondary recovery for sustainability.

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