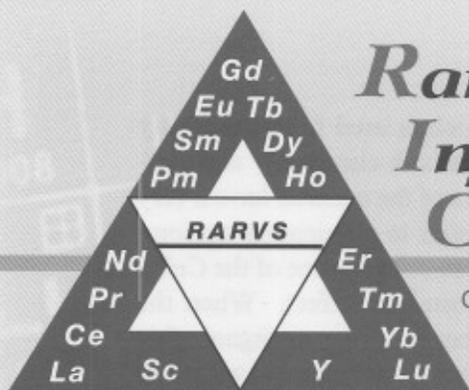


Rare-earth Information Center

Insight



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Vol. 14

February 2001

No. 2

Separating Rare Earth Elements

A recent article in *Science* on a technique for enhanced rare earth separation, "Technique for Enhanced Rare Earth Separation," produced a very favorable response in the "Perspectives: Chemical Engineering" portion of the journal (*Science*, 289, 2326-9 (2000)). The method, which involves the selective reduction and subsequent fractional distillation of rare earth chlorides, produces separation factors two orders of magnitude greater than those for liquid-liquid extraction. Both the article and the response take the viewpoint that the high separation factor of the process, which significantly reduces the number of separation steps, will result in lower costs. The process is scientifically interesting and relies on two interesting pieces of chemistry. First, the dichlorides of a number of rare earths exist, but the reduction potential of the trichloride to the dichloride is a reasonably strong function of the rare earth. Second, it is generally true that the dihalides have a vapor pressure that is one or two orders of magnitude less than that of the trihalides. (Halides are F, Cl, Br, I, At.) Thus, if a carefully selected reducing agent is added to the mixture of rare earth trichlorides, some of the rare earth trichlorides are reduced to dichlorides, while others are not. The unreduced trichlorides may then be distilled off, separating the rare earths into two groups. For model systems of Pr-Nd and Nd-Sm, the authors obtain a separation factor on the order of 600. The authors define the separation factor for the two rare earths as $\beta_{RE1/RE2} = (x_{RE1}^r/x_{RE1}^d)/(x_{RE2}^r/x_{RE2}^d)$, where x_{RE}^r is the average mole fraction in the residue left after distilling, and x_{RE}^d is the average mole fraction of the distillate. Based on this number, the authors claim a large advance in rare earth separation technology.

I am considerably less excited about the process than either the authors or Fray. In his commentary, Fray (*Science*, 289, 2295-6 (2000)) presents a diagram illustrating the conventional process, as reported by Molycorp, and states the new process requires far fewer steps. This is misleading, as the process that is diagramed starts with the ore, so that the complete elimination of the rare earth separation process only reduces the number of steps by 40%. For the separation process, the separation factor is not the only important component. In the proposed process, the chlorides must first be prepared, which involve precipitation from a solution. In the liquid-liquid process, chlorides in solution are used. The chlorides are then mixed with a reducing agent. It appears that the agent must be a pure metal, which is different for each separation. A chloride of that metal is produced in the process and must be separated out during the process. The reduction requires holding the material at 700-800°C for a number of hours. The product of this process is then vacuum distilled at around 900°C. The rates achieved in the experiments appear to be very low, so the process may involve long times at high temperatures. Finally, the product is deposited in solid form at temperatures from 600-700°C. It would appear that the proposed process is inherently a batch process. While it is true that the flow diagrams for current liquid-liquid processes are complicated, the process is continuous and well automated. The solubility of the rare earth oxides in solution is on the order of 100 gm/liter, so the rates are good. The limits of the process are floor space and capital. It appears to me that these same factors would be high for the new process, which also has rate, energy, and labor problems. For more information on processing rare earths, I would suggest the chapter by I. McGill in the *Handbook of Extractive Metallurgy*, Vol. III, F. Habashi (ed.), by Wiley-VCH, New York (1997).

Rare Earth Sunscreen

Over the past few years, the harmful effects of exposing your skin to ultraviolet rays has become well known. Sunburn is caused mainly by UV-B (290-320 nm). UV-A (320-400 nm), while not contributing very much to sunburn, does produce suntanning and can produce other detrimental changes in the skin. While the primary health hazard of UV radiation is skin cancer, other deleterious effects include accelerated aging, as evidenced by formation of wrinkles and blotches. Previously, these problems were dealt with by clothing styles that limited exposure to the sun. Currently, there is considerable demand for cosmetics that block UV. There are many organic and inorganic compounds that are effective UV blocking materials, but the requirements for cosmetics are quite stringent. First, they must be applied to the skin in moderately high concentrations without causing problems themselves. Early sunscreens used PABA, but that material was found to have deleterious effects on some people, and current sunscreens are frequently clearly marked as being PABA free. Many UV blockers have high catalytic activity, which is also undesirable, in that it may either cause undesirable reactions on the skin or accelerate the breakdown of the organic carrier used in applying the blocker. Inorganic materials, such as TiO_2 , ZnO , and more recently CeO_2 , must be in the form of fine powders for suspension in the cosmetics. In addition to behaving well as UV blockers, cosmetics must satisfy requirements on appearance and feel. When was the last time you saw a lifeguard on *Baywatch* with a white nose due to ZnO ? CeO_2 is becoming more prominent in UV blocking cosmetics, but fine CeO_2 particles readily agglomerate producing a grainy feel, which is unacceptable. CeO_2 is also an excellent catalyst, which is not good in this application. Recently, T. Masui et al. {*J. Mater. Chem.*, **10**, 353-7 (2000)} have coated CeO_2 particles with a 10 nm

layer of BN. BN, which is used for high quality crucibles, is very stable both chemically and thermally, and fine powders of the material have a very slippery feel. In addition to eliminating agglomeration, the BN passivates the surface of the CeO_2 , greatly reducing the catalytic effect. When the coated particles are incorporated in an organic thin film, the film had higher transparency and was more effective in blocking UV than TiO_2 or ZnO , which are commonly used. As the coated powders were produced using wet chemistry, mass production should not be a problem.

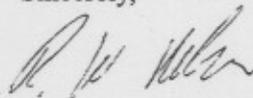
Short Notes

Magnews, The international newsletter of The UK Magnetics Society, has published a complete synopsis of the USDOE workshop on nanocomposite magnets held in Santa Fe, NM, 7-11 November 2000. The synopsis was courtesy of David Brown, Magnequench Technology Center (Email: dbrown@mqii.com). For more information on the *Center for Synthesis and Processing in Nanocomposite Magnets Workshop*, contact S. D. Bader (Email: bader@anl.gov)

NdFeB Magnets and NdFeB Magnet Systems 2001 is to be held May 14-16, 2001, in Atlanta, Georgia. Contact Chris Jones at Gorham Advanced Materials. Telephone: 207-892-5445; Fax: 207-892-2210; Email: gorham@goradv.com, Web site: www.goradv.com.

Effective January 1, 2001, Rhodia Rare Earths changed its name to Rhodia Electronics and Catalysis. The renamed Rhodia Group enterprise will be structured around three business units: Catalysis, Electronics, and New Markets.

Sincerely,



R. W. McCallum
Director of RIC