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TESE DE DOUTORADO

FRACIONAMENTO DE TERRAS RARAS COM OBTENÇÃO DE PRODUTOS DE ELEVADA PUREZA

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Carlos Antônio de Morais

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de Pós-Graduação em Engenharia Metalúrgica
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"Cuando la sociedad es rica, la gente no tiene que trabajar con las manos y se dedica a la actividad intelectual. Hay cada vez más universidades y cada vez más estudiantes. Los estudiantes, para poder terminar sus carreras, tienen que inventar temas para sus tesinas. Hay una cuantidad infinita de temas, porque sobre cualquier cosa se puede hacer un estudio. Los folios de papel escrito se amontonan en los archivos, que son más tristes que un cementerio, porque en ellos no entra nadie, ni siquiera el día de los difuntos. La cultura sucumbe bajo el volumen de la producción, la avalancha de las letras, la locura de la cuantidad."

Milan Kundera - "La Insoportable Levedad del Ser"

A publicação em revistas, em especial naquelas de circulação internacional, nos salva dos tristes arquivos mencionados pelo autor.

À minha esposa Floraci,
à minha filha Bianca e
ao meu filho Leonardo

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RESUMO

O presente trabalho teve como objetivo a obtenção de óxidos de terras raras (lantânio, európio e gadolínio) de alto grau de pureza, a partir de misturas naturais desses elementos. O estudo de obtenção do európio foi realizado utilizando as técnicas de redução química e redução fotoquímica. O óxido de lantânio (La_2O_3) foi obtido pela técnica de extração por solventes, a partir de uma solução clorídrica de terras raras leves. O óxido de gadolínio (Gd_2O_3) foi obtido por precipitação, a partir do sobrenadante do processo de recuperação do európio.

Para o estudo da recuperação do európio via redução química foram adotadas duas abordagens. A primeira, envolvendo a utilização de uma mistura de elementos terras raras médias e pesadas, levou à obtenção do óxido de európio (Eu_2O_3) com pureza de 99.4 %. O produto acima foi obtido em duas etapas de redução/precipitação, a partir de uma amostra contendo 2,4 g L^{-1} Eu_2O_3, 114,4 g L^{-1} Sm_2O_3, 64,2 g L^{-1} Gd_2O_3, 0,81 g L^{-1} Nd_2O_3, 4,10 g L^{-1} Tb_4O_7 e 1,45 g L^{-1} Y_2O_3. A segunda abordagem envolveu a separação prévia do samário por extração por solventes, seguida da recuperação do európio via redução química/precipitação. Neste caso foi obtido um produto com pureza de 99,99 %, também em duas etapas de redução/precipitação, a partir de uma amostra contendo 5,0 g L^{-1} Eu_2O_3 e 143,2 g L^{-1} Gd_2O_3. O rendimento do processo foi de 94%. A recuperação posterior do gadolínio presente no sobrenadante do processo de recuperação do európio, levou à obtenção do óxido de gadolínio, (Gd_2O_3) 99,6%. O produto foi obtido mediante precipitação do gadolínio como oxalato e posterior calcinação a 900^{o}C.

A recuperação do európio pela técnica de redução fotoquímica/precipitação foi avaliada na presença de íons sulfato e de removedor do radical hidroxila. Como fonte de irradiação, foram utilizadas duas lâmpadas de mercúrio de baixa pressão, com emissão em 253,7 nm. Nos estudos realizados com uma solução pura de cloreto de európio, obteve-se uma recuperação de 99 % do európio, precipitado na forma de sulfato de európio II ($EuSO_4$). Na solução contendo elevada concentração de gadolínio (relação

molar Gd/Eu de 27), observou-se a precipitação dos dois elementos sem seletividade na separação.

Na tentativa de se obter soluções mais puras e concentradas em európio para alimentar o processo de redução química foi estudada a separação Eu/Gd por extração por solventes. Foram avaliadas duas rotas do processo. A primeira, visando a extração do európio, foi realizada com extratantes básicos (aminas). Nesse procedimento, o extratante mais promissor foi o Aliquat 336® na forma de nitrato (nitrato de tricaprilmetilamônio), com o qual foi obtido um fator de separação Eu/Gd de 2,0. A segunda rota, visando a extração parcial do gadolínio, foi realizada com extratantes ácidos. Nesse caso, o EHE(EHP) (ácido 2-etilhexilfosfônico mono-2-etilhexil éster) apareceu como o extratante mais indicado, com um fator de separação Eu/Gd de 1,59, contra 1,44 obtido com o DEHPA (ácido di-2-etilhexilfosfórico).

O estudo de fracionamento dos elementos de terras raras leves (La, Pr, Nd), pela técnica de extração por solventes foi realizado com dois extratantes ácidos: DEHPA e EHE(EHP). Nesse estudo, o EHE(EHP) apresentou os melhores resultados, com fatores de separação de 10,2 e 1,33, para os pares La/Pr e Pr/Nd, respectivamente, contra 5,42 e 1,10 obtidos com o DEHPA. Ensaios contínuos realizados com EHE(EHP) em uma bateria de misturadores/decantadores, levou à obtenção de óxido de lantânio (La_2O_3) com pureza superior a 99,9 % em 16 estágios de misturadores/decantadores, sendo 8 estágios de extração e 8 estágios de lavagem. O estudo foi realizado com uma amostra de cloreto de terras raras leves contendo 32,8 g L^{-1} La_2O_3, 6,62 g L^{-1} Pr_6O_{11} e 25,2 g L^{-1} Nd_2O_3. A recuperação obtida no processo foi de 99,9%.

ABSTRACT

The work describes the development of processes to obtain high-grade rare earth oxides (La, Eu and Gd), from a natural mixture of these elements. The production of europium oxide (Eu_2O_3) was carried out by chemical reduction and photochemical reduction techniques. The lanthanum oxide (La_2O_3) was recovered from a light rare earth chloride solution by using solvent extraction. The gadolinium oxide (Gd_2O_3) was obtained by precipitation from the supernatant of the process of europium recovery.

Two approaches were applied to the recovery of europium by chemical reduction. The first one involved the use of a mixture of middle and heavy rare earth elements. A product assaying 99.4% Eu_2O_3 was obtained with a recovery of 92% from a rare earth chloride solution containing 2.4 g L^{-1} Eu_2O_3, ll4.4 g L^{-1} Sm_2O_3, 64.2 g L^{-1} Gd_2O_3, 0.81 g L^{-1} Nd_2O_3, 4.10 g L^{-1} Tb_2O_3 and 1.45 g L^{-1} Y_2O_3 in two stages of reduction/precipitation. The second approach involved a previous separation of samarium by solvent extraction, followed by europium recovery using chemical reduction/precipitation. A product assaying 99.99% Eu_2O_3 was obtained also in two stages of reduction/precipitation, from a sample containing 5.0 g L^{-1} Eu_2O_3 and 143.2 g L^{-1} Gd_2O_3. The process yield was 94%. The subsequent gadolinium recovery from the supernatant of the europium precipitation process led to a 99.6% pure Gd_2O_3. The product was obtained by precipitation of gadolinium as oxalate and further calcination at 900^{o}C.

The europium recovery by photochemical reduction/precipitation was evaluated in the presence of sulfate ions and hydroxyl radical scavengers. Two low-pressure mercury lamps of 15 W, with emission peak at 253.7 nm were used as the irradiation source. The europium recovery (as $EuSO_4$) from a pure europium chloride solution was of 99%. When precipitation was carried out from a solution enriched in gadolinium (Gd/Eu=27) no selectivity was achieved, owing to Eu-Gd co-precipitation.

The separation Eu/Gd by solvent extraction was studied as an attempt to generate purer and more concentrated europium solution to feed the chemical reduction process described above. Two process routes were evaluated. The first one, aiming at extracting europium, was carried out with basic extractants (amines). By this procedure the best results were obtained with Aliquat 336® in nitrate form (tricaprylylmethylammonium nitrate), from a Eu/Gd nitrate solution. The Eu/Gd separation factor was equal to 2.0. The second route, aiming at a partial gadolinium extraction, was carried out with acid extractants: EHE(EHP) (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) and DEHPA (di-2-ethylhexilphosphoric acid). The best results were obtained with EHE(EHP) as indicated by a Eu/Gd separation factor of 1.59, against 1.44 with DEHPA.

The separation of light rare earth elements (La, Pr, Nd) by solvent extraction was carried out by using DEHPA and EHE(EHP) as extractants. The best results were also obtained with EHE(EHP), as indicated by separation factors of 10.2 and 1.22, respectively for the pairs La/Pr and Pr/Nd. The separation factors obtained with DEHPA were 5.42 for La/Pr and 1.10 for Pr/Nd. Continuous counter-current solvent extraction trials with EHE(EHP) in a mixer/settler battery led to La_2O_3 over 99.9% pure. This product was recovered in 16 stages of mixer/settler, 8 extraction stages and 8 scrubbing stages, from a light rare earth chloride solution containing 32.8 g L^{-1} La_2O_3, 6.62 g L^{-1} Pr_6O_{11} and 25.2 g L^{-1} Nd_2O_3. The process yield was 99.9%.

CAPITULO 1

1. INTRODUÇÃO

1.1. OS ELEMENTOS TERRAS RARAS

De acordo com a IUPAC ("*International Union of Pure and Applied Chemistry*"), são chamadas terras raras (TR) o conjunto dos elementos da série do lantânio (La), com números atômicos de 57 a 71, mais o ítrio (Y) e o escândio (Sc). Outra terminologia também muito aplicada para a série do lantânio é o termo "Lantanídeos" (série dos lantanídeos). Porém, pela IUPAC, o lantânio não faz parte desta série. Também, contrariando a IUPAC, muitos autores têm excluído o escândio da série dos elementos terras raras, colocando-o na série do alumínio [1,2].

Os elementos terras raras apresentam propriedades químicas e físicas muito parecidas e ocorrem na natureza juntos, em proporções variadas, em diversas fontes minerais. As propriedades químicas dos elementos terras raras, à exceção do ítrio e escândio, são marcadas pelo fenômeno conhecido como contração lantanídica, isto é, ao longo da série, os valores dos raios iônicos destes elementos diminuem de forma suave e contínua. Esta contração se deve ao aumento na carga nuclear, que não é completamente blindada pela adição de elétrons 4f que aumentam escalonadamente de uma unidade na série dos lantanídeos. Este aumento efetivo na carga faz com que os elétrons se aproximem do núcleo, diminuindo assim o raio iônico à medida que o número atômico aumenta. A contração lantanídica é responsável pela pequena diferença de basicidade existente entre os elementos terras raras, que decresce no mesmo sentido que o raio iônico decresce [1-3]. A química destes elementos é essencialmente iônica, com todos eles formando cátions trivalentes (TR^{3+}). Embora a valência (III) seja predominante, alguns destes elementos podem apresentar valência (II) (TR^{2+}) e valência (IV) (TR^{4+}), porém com menor estabilidade que os cátions trivalentes. Os íons bivalentes e tetravalentes são formados pelos elementos que podem alcançar uma configuração eletrônica mais estável em relação à inicial, onde se tem os orbitais 4f vazios ($4f^{0}$), semi completos ($4f^{7}$) ou completos ($4f^{14}$). Desta forma, têm-se espécies como Ce^{4+} e Tb^{4+}(configurações $4f^{0}$ e $4f^{7}$ respectivamente) e Eu^{2+} e Yb^{2+} (configurações $4f^{7}$ e $4f^{14}$ respectivamente). Existem também elementos, como La, Gd, Lu, Y e Sc, que só formam espécies trivalentes, onde a retirada dos três elétrons conduz à configuração de gás nobre (La, Y e Sc) ou aos estados estáveis $4f^{7}$ e $4f^{14}$ (Gd e Lu) [1,2].

As espécies Pr^{4+} e Sm^{2+}, formadas a partir das respectivas espécies trivalentes, mediante perda e ganho de um elétron, respectivamente, podem em raros casos obter uma estabilidade extra. Nestes dois casos, Pr e Sm tendem para os níveis vazio ou semi-completo respectivamente [3].

1.2. OCORRÊNCIA

O nome terras raras foi dado pelo sueco Lieutenant Arrhenius, que as descobriu no final do século XVIII em cavernas da Suécia. Este nome se deve ao fato de sua ocorrência na forma de óxidos ou com aparência de óxidos (“terras” na antigüidade) e por pensar se tratar de um tipo de “terras” muito raro. Com o tempo, os pesquisadores descobriram que estes óxidos se distribuem amplamente pela crosta terrestre, estando presentes em mais de 100 minerais. A concentração média dos elementos de terras raras em conjunto somam em torno de 150 $\mu g\ g^{-1}$ na crosta terrestre estando presentes em maior abundância que vários elementos comuns, como o Cu (70 $\mu g\ g^{-1}$), Sn (40 $\mu g\ g^{-1}$), Pb (16 $\mu g\ g^{-1}$), Mo (9 $\mu g\ g^{-1}$), dentre outros [4,5].

Os principais depósitos minerais, a partir dos quais são extraídas as terras raras, encontram-se na China, Estados Unidos, Austrália, Índia, Brasil, Canadá, Países Escandinavos e nos países da antiga União Soviética. Dentre os minerais de terras raras, destacam-se a bastnaesita, a monazita e a xenotima, sendo a monazita o mais importante deles [1-4,6]. No Brasil, as ocorrências de TR são numerosas, com reservas geológicas importantes. Os três depósitos principais do país encontram-se no Planalto de Poços de Caldas (MG), em Catalão (GO) e no Complexo Carbonatítico de Araxá (MG). Os recursos contidas nesses depósitos totalizam 3,26 milhões de toneladas, com teores em óxido de terras raras (TR_2O_3) de 3,9 %, 10 % e 6,3 %, respectivamente. Essas reservas aumentam substancialmente quando se considera as TR associadas a outros minerais, como anatásio, apatita, fluorita, cassiterita, dentre outros. Os teores dos elementos TR presentes nesses minerais no Brasil variam entre 1 a 2 %, o que pode viabilizar sua recuperação como subproduto [4].

1.3. APLICAÇÃO

As aplicações dos elementos de terras raras têm crescido muito nos últimos anos. Atualmente, esses elementos são de vital importância no desenvolvimento tecnológico e industrial, com aplicações em diversas áreas da Engenharia Química, Engenharia Metalúrgica, Engenharia de Materiais, nas áreas nuclear, aeronáutica, eletrônica, dentre outras. As terras raras têm poucas aplicações na forma de mistura. Suas aplicações mais nobres estão ligadas à pureza dos respectivos óxidos individuais [1,2,4,7-9].

Dentre os diversos campos de aplicação industrial das terras raras pode-se citar:

- metalurgia: aço especiais, ligas metálicas e produtos pirofóricos;
- catálise: craqueamento do petróleo e escapamento de veículos (antipoluentes);
- cerâmica: indústria eletrônica, micro-eletrônica, eletroótica (fibras óticas) e na coloração de refratários;
- vidros: polimento, ótica, descoloração e coloração, controle de radiações, fluorescência e revestimento;
- supercondutores;

- magnetos permanentes (Sm-Co, Nd-Fe-B);
- “fósforos” (emissões de comprimento de onda específicos): tubos de raios catódicos, telas de raios-X, lâmpadas fluorescentes e lasers;
- energia nuclear, especialmente no caso do gadolínio, como absorvedor de neutrons;
- hidretos metálicos;
- sensores de oxigênio;
- sistemas de células de memória;
- medicina;
- outros (pigmentos, joalheria, sistemas de energia solar, microondas, refrigeradores, feixes microscópicos, nutrientes agrícolas, etc.).

1.4. MÉTODOS DE DETERMINAÇÃO

Os métodos utilizados para a determinação dos elementos terras raras podem ser divididos em dois grupos, denominados de métodos clássicos e métodos espectrométricos. São considerados clássicos os métodos gravimétricos, volumétricos e espectrofotométricos. Os métodos gravimétricos e volumétricos são mais comumente empregados para a determinação do teor das terras raras totais. Dependendo das faixas de teores, alguns desses elementos podem ser determinados individualmente por espectrofotometria de absorção molecular. Com exceção do La, Lu e Y, todos os demais elementos terras raras absorvem luz na região do visível e ultra violeta próximo. As determinações por esta técnica, geralmente, são conduzidas em meio clorídrico ou perclórico [1,2,8].

Dentre os métodos espectrométricos ou instrumentais pode-se citar a espectrometria de absorção atômica, espectrometria de emissão atômica em plasma e fluorescência de raios-X. Esses métodos apresentam como vantagem a possibilidade da determinação dos elementos individuais. Porém, não são os únicos métodos utilizados na determinação das terras raras. Além desses, outros métodos como cromatografia líquida, ativação neutrônica, eletroforese capilar, são também empregados na determinação destes elementos [1,2,8,10].

Neste trabalho foram utilizados os métodos clássicos, gravimétrico e volumétrico e os métodos instrumentais de fluorescência de raios-X (espectrometria de energia de raios-X) e de espectrometria de emissão atômica com plasma indutivamente acoplado (ICP/AES). No método gravimétrico, os elementos terras raras foram precipitados na forma de oxalato, via adição de solução de ácido oxálico 10 % p/v e, quando necessário, com a adição de hidróxido de amônio para ajuste do pH e posterior calcinação a 900^0C por 1 hora. No método volumétrico, as terras raras foram determinadas por titulação, utilizando solução de EDTA (ácido etilenodiaminotetraacético), como agente complexante (solução titulante), solução tampão de acetato de sódio (1 mol L^{-1})/ácido acético (pH 5,5) e o alaranjado de xilenol como indicador. De modo geral, os métodos clássicos foram utilizados para confirmação de análise, onde os elementos foram determinados individualmente por outro método, ou na determinação de algum elemento em solução pura do mesmo. A espectrometria de emissão atômica em plasma foi utilizada em algumas determinações específicas para a determinação de impurezas e confirmação de alguns resultados.

O acompanhamento do desenvolvimento dos processos citados neste trabalho foi realizado utilizando-se a técnica de espectrometria de energia de raios-X, sistema Kevex. A espectrometria de energia de raios-X é uma variante da fluorescência convencional, onde os raios-X são gerados por um radioisótopo, neste caso, o amerício (Am^{241}). O elemento básico da espectrometria de energia de raios-X é o detector de estado sólido [Si(Li)], onde a deposição da energia de um fóton incidente resulta em um pulso elétrico de altura proporcional à energia do fóton. O fóton detectado é registrado no analisador multicanal que então soma 1 à contagem do canal referente àquela energia. Este processo resulta no espectro de energia de raios-X.

A alta eficiência de detecção dos detetores de estado sólido e a alta eficiência geométrica permitem o uso de feixes de fótons de intensidade relativamente baixa para a excitação de raios-X característicos, tal como são as fontes disponíveis de certos isótopos radioativos. Especificamente, para a análise de elementos terras raras, Am^{241} é o radioisotopo indicado como fonte de produção de fluorescência. O espectro de raios-X é formado devido à excitação da camada K do átomo, que produz espectros simples comparados aos da série L, normalmente obtidos na espectrometria convencional de fluorescência de raios-X (denominada espectrometria por dispersão de comprimento de onda). Outra vantagem do sistema Kevex, é o fato das análises serem conduzidas em amostras sólidas ou líquidas, com baixos limites de detecção. Neste caso, o limite de detecção depende do tempo de contagem e do número atômico do elemento. Para os elementos terras raras, este limite pode chegar a poucos de microgramas por grama [11-17].

1.5. PROCESSOS DE SEPARAÇÃO

A separação de espécies químicas, em geral, e dos elementos terras raras, em particular, tem recebido desde a antigüidade uma grande atenção por parte dos pesquisadores. Isso, devido à crescente necessidade de se aumentar a pureza dos produtos obtidos.

Como mencionado anteriormente, os íons trivalentes dos elementos terras raras apresentam um comportamento químico muito similar, o que torna a obtenção destes elementos individuais, a partir de fontes naturais, em separações das mais complexas da química inorgânica.

Os vários processos de separação individual das terras raras, a partir da ocorrência natural, utilizam essencialmente a pequena diferença de basicidade resultante do decréscimo do raio iônico destes elementos, que ocorre no sentido do lantânio para o lutécio. A diferença de basicidade é responsável pela diferença de solubilidade de seus sais, pela hidrólise dos íons e pela formação dos complexos destes elementos. As técnicas de separação mais utilizadas são: cristalização fracionada, oxidação e redução, cromatografia, membrana líquida, troca iônica e extração por solventes. [1,2,6,8,9]. Recentemente, vários estudos de separação de terras raras, vem utilizando o processo químico de transporte de vapor [18-26]

A técnica de cristalização fracionária baseia-se na diferença de solubilidade dos respectivos sais, geralmente na forma de sulfatos. Os fatores de separação são muito próximos de 1, sendo necessárias numerosas etapas de cristalização. Esta técnica foi aplicada até meados do século XX, quando foi substituída pelas técnicas de troca iônica e de extração por solventes [1,3,6].

As técnicas de oxidação e redução são aplicadas na separação do cério e európio, respectivamente [6,8]. Em meio básico, o cério trivalente (Ce^{3+}) é facilmente oxidado ao estado tetravalente (Ce^{4+}), ocorrendo mesmo durante a secagem do hidróxido de terras raras na presença de ar. Em meio ácido, a transformação do Ce^{3+} a Ce^{4+} só ocorre na presença de oxidantes fortes, tais como persulfato, bismutado, bromato, etc. [8,27]. A separação por esta técnica baseia-se na diferença entre os produtos de solubilidade do hidróxido de Ce(IV) ($Ce(OH)_4$) e dos hidróxidos dos demais elementos no estado trivalente ($TR(OH)_3$). Os produtos de solubilidade dos hidróxidos dos elementos trivalentes ($TR(OH)_3$ variam de 10^{-19} ($La(OH)_3$) a $10^{-23,7}$ ($Lu(OH)_3$), enquanto o produto de solubilidade do $Ce(OH)_4$ é da ordem de 10^{-51} [8,28,29]. Quando a oxidação ocorre em meio ácido, o $Ce(OH)_4$ é precipitado preferencialmente aos demais hidróxidos. Quando se precipita a mistura de hidróxidos trivalentes e, durante a secagem deste produto, o Ce(III) é oxidado a Ce(IV), assim o $Ce(OH)_4$ permanece insolúvel, quando o sólido é lixiviado com ácido diluído [8].

O Eu(III) é facilmente reduzido a Eu (II). Esta conversão pode ser realizada por redução química, eletroquímica ou fotoquímica. Devido à baixa estabilidade do íon Eu(II), em meio aquoso, este deve ser rapidamente removido da solução. Essa remoção geralmente é feita via precipitação do európio divalente como sulfato ($EuSO_4$) [30-34].

As técnicas de cromatografia líquida e membrana líquida apresentam grande aplicação na química analítica. Por meio dessas técnicas, é possível concentrar elementos traços e eliminar interferentes. Com base neste potencial, essas técnicas são também aplicadas na separação individual das terras raras, em pequena escala [2,35-42].

Foi a partir da Segunda Guerra Mundial que começaram a ser desenvolvidas as técnicas de troca iônica e extração por solventes para a separação das terras raras. No início dos anos 50 do século XX, J. E. Powell Spedding e colaboradores mostraram que era possível separar grandes quantidades dos elementos de terras raras, obtendo-os em alta pureza, e tornando-os assim, disponíveis para usos especializados, como na eletrônica, em substâncias fluorescentes e na indústria ótica [3].

As técnicas de extração por solventes e de resinas trocadoras de íons são fundamentadas nos mesmos princípios químicos, mas diferem nos princípios tecnológicos. A extração por solventes, também conhecida como extração líquido-líquido apresenta vantagens, como maior velocidade de transferência de massa e vantagens econômicas, como equipamentos e tempo de processo menores. As resinas têm velocidade de transferência de massa menor e necessitam de equipamentos e tempos de processo maiores [35].

O processo de troca iônica tem sido utilizado na produção de terras raras mais puras. Foi a técnica que substituiu a cristalização fracionada e, embora, há alguns anos, venha sendo também substituída pela técnica de extração por solventes, ainda é utilizada na purificação final desses elementos [1]. As resinas trocadoras de íons podem ser classificadas em resinas catiônicas, resinas aniônicas e resinas quelantes. No caso específico das terras raras, as resinas catiônicas são as mais empregadas. As resinas podem também ser utilizadas na forma impregnada com extratantes líquidos [43-49].

Atualmente, a técnica de extração por solventes tem sido largamente utilizada na separação dos elementos terras raras em escala industrial. Essa técnica pode ser descrita de maneira simples através da reação:

$$M_{(aq)} + E_{(org)} = ME_{(org)} \qquad (1.1)$$

onde $M_{(aq)}$ corresponde à espécie a ser extraída na fase aquosa e $E_{(org)}$ representa o extratante orgânico.

Na primeira etapa do processo de extração, a espécie de interesse é transferida da fase aquosa para a fase orgânica mediante ação do extratante, E_{org}, formando-se o complexo ME_{org}. Na segunda etapa, chamada de reextração, ocorre a reação inversa da primeira. Nessa etapa, a espécie previamente extraída é transferida para uma segunda fase aquosa. Geralmente, entre as etapas de extração e reextração utiliza-se uma etapa de lavagem, onde espécies não desejadas, parcialmente extraídas, retornam para a fase aquosa. Muitas vezes a seletividade do processo é determinada por esta etapa.

Os estudos de extração por solventes dos elementos terras raras, iniciados em meados do século passado, continuam sendo extensivamente realizados até os dias de hoje. Esses focalizam a extração em diferentes meios e com diversos extratantes, como os derivados dos ácidos fosfatados (ácido fosfórico, fosfônico e fosfínico), com destaque para o ácido di-2-etilhexilfosfórico (DEHPA) e o ácido 2-etilhexilfosfônico mono-2-etilhexil éster (HEH(EHP)) [50-69], os fosfatos neutros, como o tri-n-butilfosfato (TBP) e o tri-n-octilfosfato (TOPO) [54, 69-76], os derivados do ácido carboxílico [54,58,68, 77-79], as aminas [58, 80-87], além das cetonas, oximas e outros [83-93].

Apesar do grande número de estudos sobre a extração dos elementos terras raras existem poucas informações em literatura sobre os processos de separação desses elementos, ressaltando-se neste caso, as publicações de Preston [51,80], Thakur *et al* [52], Santos *et al* [53] e Miranda e Ziner [54]. A grande maioria desses estudos enfocam aspectos teóricos envolvidos na extração, como fator de separação, mecanismos de extração, estudos cinéticos, coeficiente de distribuição, dentre outros. Das classes de extratantes citados anteriormente, os extratantes ácidos, derivados dos ácidos fosfatados, são os mais empregados nos processos de separação das terras raras. Dentre esses, o DEHPA e o HEH(EHP), derivados dos ácidos fosfórico e fosfônico, respectivamente, são os mais utilizados. O DEHPA apresenta um coeficiente de extração maior que o HEH(EHP), mas em contrapartida, possui menor seletividade e, devido a estas características, é mais utilizado na separação dos elementos terras raras por grupos e na separação de elementos não adjacentes [51,55]. O HEH(EHP), por apresentar menor coeficiente de extração, tem como vantagem, além da maior seletividade, maior facilidade de reextração. Porém, esta reextração para as terras raras pesadas, onde a interação HEH(EHP)-TR é maior, ainda requer elevadas concentrações de ácido (HCl ~ 6 mol/L) [56]. Os derivados do ácido fosfínico, representados pela linha "Cianex®", como Cianex 272, Cianex 302, Cianex 923, não têm sido empregados comercialmente na separação das terras raras devido à baixa capacidade de carregamento e ao baixo coeficiente de distribuição. Porém, a mistura HEH(EHP) e Cianex favorece a reextração das terras raras, sem perder a seletividade, a capacidade de carregamento e o coeficiente de distribuição do HEH(EHP) [56].

Os extratantes ácidos são trocadores catiônicos, cujo o hidrogênio ácido é substituído pelo íon metálico. A introdução de íons H^+ na fase aquosa desfavorece a extração, sendo em alguns casos necessário fazer ajustes do pH nesta etapa do processo. Uma outra alternativa que vem sendo aplicada é a utilização do HEH(EHP) saponificado [52,53]. Porém, nesse caso, deve-se levar em consideração a degradação do solvente na etapa de saponificação.

O TBP, muito empregado no passado na separação das terras raras, é utilizado em meio nítrico. Apresenta como desvantagens a elevada acidez e a alta concentração de nitrato necessárias na fase aquosa [70-73]. Outro extratante neutro utilizado na separação das terras raras é o TOPO. Porém, o TOPO é mais empregado em mistura com outros extratantes, com o objetivo de aumentar o efeito sinergítico na etapa de extração [56,74,91].

A ordem de extração na série dos lantanídeos tanto para os extratantes ácidos, como os neutros, derivados dos fosfatos, cresce com o aumento do número atômico, ou seja, o coeficiente de extração aumenta no sentido La – Lu [57-59, 71,72,75].

Dentre os extratantes derivados do ácido carboxílico, destacam-se os ácidos versático e nafiténico. As características de extração dos lantanídeos, pelos diferentes derivados do ácido carboxílico, podem ser relatadas pelo parâmetro estérico do grupo alquil substituinte. Para o ácido versático 10®, em meio nítrico, o comportamento é o inverso do observado para os ácidos fosfatados, ou seja, o coeficiente de extração decresce no sentido La – Lu [77,78].

Os extratantes contendo o grupo amino, mais utilizados nos processos de separação das terras raras por extração por solventes, são o Primene JM-T®, o Primene 81R® (aminas primárias), a Alamina 336® (amina terciária) e os sais quaternários de amônio, com destaque para nitrato de tricaprilmetilamônio (Aliquat 336® na forma de nitrato) e o nitrato de tri-n-octilmetilamônio (TOA). As aminas extraem via seus sais formados pela prévia protonação dessas. Os sais de aminas extraem espécies aniônicas ou neutras, por troca aniônica ou formação de adutos, respectivamente. Desta forma, esses extratantes devem ser utilizados em um meio aquoso que favoreça a formação de complexos aniônicos ou neutros. As aminas primárias são utilizadas na extração de terras raras em meio sulfúrico [69]. A Alamina 336 e os sais quaternários de amônio, geralmente, são utilizados em meio nítrico. Porém, esses extratantes podem ser também utilizados em outros meios, como em tiocianato. Em meio nítrico, a ordem de extração dos lantanídeos pelo Aliquat 336 na forma de nitrato decresce com o aumento do número atômico, enquanto em tiocianato, essa ordem é invertida [58]. A ordem de extração pelo TOA em meio nítrico também decresce com o aumento do número atômico [80-83].

Outra classe de extratantes utilizados na extração das terras raras são as cetonas, sendo mais comuns as representadas pela série “LIX®”, como LIX 51, LIX 54, LIX 70. O coeficiente de extração desses extratantes aumenta com o aumento do número atômico dos lantanídeos [83,86,88]. As cetonas têm sido utilizadas em misturas com aminas, visando aumentar o coeficiente de extração destas [83, 84-87]. A modificação das aminas, pela adição de β-dicetonas, tem sido realizada no sentido de melhorar a extração e a separação das fases aquoso/orgânico. O grau de aumento da extração cresce com o aumento do número atômico dos lantanídeos [86].

A separação dos elementos terras raras envolve inicialmente a separação em grupos. Nesta etapa obtém-se os concentrados de TR leves (La, Ce, Pr, Nd), TR médias (Sm, Eu, Gd) e TR pesadas (Tb, Dy, Ho, Er, Tm, Lu, Y, Sc). Esta separação, geralmente, realizada utilizando o DEHPA como extratante, é favorecida pelos maiores fatores de separação entre Nd/Sm e Gd/Tb, comparados com os fatores de separação dos demais elementos adjacentes [3]. Os elementos de TR individuais são posteriormente separados e purificados por extração por solventes ou troca iônica [1].

O estudo dos fatores de separação é de fundamental importância na escolha do sistema a ser utilizado nos processos de separação das terras raras. Sato [57], em seu estudo de separação das terras raras em meio clorídrico, realizado com os extratantes DEHPA e HEH(EHP) determinou os fatores de separação, para todos os lantanídeos. Para os contemplados no presente trabalho (La, Pr, Nd, Eu e Gd), os fatores de separação encontrados foram: sistema TR(III)-HCl-DEHPA - Pr/La = 2,18, Nd/Pr = 1,06 e Gd/Eu = 1,69; sistema TR(III)-HCl-HEH(EHP) - Pr/La = 1,42, Nd/Pr = 1,17 e Gd/Eu = 1,46

Li [63] investigou os fatores de separação das terras raras em meio clorídrico e nítrico, utilizando como extratantes o Cianex 272 e o Cianex 302. Para o sistema TR(III)-HCl-Cianex 272, foram encontrados os seguintes fatores de separação, para os elementos de interesse em nosso estudo: Pr/La = 39,7, Nd/Pr = 1,3 e Gd/Eu = 1,16. Para o sistema TR(III)-HNO_3-Cianex 302, os fatores de separação encontrados para esses pares foram: Pr/La = 10,5, Nd/Pr = 1,40 e Gd/Eu = 1,74.

Yamagughi [67] estudou a separação do par Nd/Pr em meio clorídrico, com o DEHPA, na presença dos agentes complexantes EDTA (ácido etilenodiaminotetraacético) e DTPA (ácido dietilenotriaminopentaacético), na presença de campo elétrico. Neste caso foi observado uma variação do fator de separação Nd/Pr de 1,2 a 1,9, quando a concentração de EDTA variou de 0,5 a 0,9 mol/L. Para o DTPA na concentração de 0,9 mol/L, o fator de separação foi semelhante ao obtido na presença do EDTA nesta concentração.

Cecconie e Freiser [75] investigaram a extração dos elementos La(III), Pr(III), Eu(III), Tb(III), Ho(III) e Yb(III) em meio clorídrico com TOPO diluído em clorofôrmio. O fator de separação encontrado para o par Pr/La nesse sistema foi de 1,51.

Preston [80] descreve os fatores de separação dos elementos terras raras adjacentes em meio nítrico para o Aliquat 336® na forma de nitrato, o DEHPA e o EHE(EHP). Os fatores de separação citados para o par Nd/Pr foram: 2,04, 1,27 e 1,25 para o Aliquat, o HEH(EHP) e o DEHPA, receptivamente. Para o par Gd/Eu os fatores mencionados foram: 1,75, 1,35 e 1,50, também para o Aliquat, o HEH(EHP) e o DEHPA, receptivamente.

Neste trabalho foram utilizadas as técnicas de extração por solventes e de redução/precipitação. A técnica de extração por solventes foi empregada no estudo de fracionamento das terras raras leves e nos estudos de separação de Eu(III)/Gd(III). O estudo de fracionamento das terras raras leves foi realizado em meio clorídrico, com os extratantes DEHPA e EHE(EHP). O estudo de separação do par Eu(III)/Gd(III) foi realizado com extratantes ácidos e básicos. Os extratantes ácidos investigados foram o DEHPA e o EHE(EHP) saponificado e não saponificado em meio clorídrico. Como extratantes básicos foram investigados o Primene JM-T, o Primente 81R, a Alamina 336, o Aliquat 336 na forma de cloreto e o Aliquat 336 na forma de nitrato. O estudo com os extratantes básicos foram realizados em meio sulfúrico, clorídrico e nítrico. A técnica de redução/precipitação foi empregada na recuperação do európio. O estudo de redução do európio foi realizado com duas amostras, uma contendo os elementos do grupo das terras raras médias (Sm, Eu e Gd) além de outros elementos, como Nd, Tb e Y, e outra contendo contento somente a mistura de Eu e Gd. Os estudos de fracionamento das terras raras leves, com obtenção do lantânio de elevada pureza, foram realizados com uma amostra contendo La, Pr e Nd. Todas as amostras foram fornecidas pela INB – Indústrias Nucleares do Brasil S/A.

1.6. RELEVÂNCIA

A obtenção dos elementos terras raras individuais é praticada por alguns países, mas esta tecnologia não está disponível. As informações de literatura não evidenciam as condições de separação, ou seja, para o domínio dessa tecnologia, torna-se necessário uma pesquisa bastante ampla dos parâmetros de processo.

No Brasil, o processo de separação e purificação dos elementos terras raras ainda não é praticado industrialmente e, embora vários estudos tenham sido realizados, existem poucas publicações referentes a estas pesquisas. Estas informações ficam limitadas aos próprios setores de pesquisa ou aos pesquisadores.

O Brasil possui reservas significativas de terras raras e, atualmente, o domínio da tecnologia de separação já se caracterizou como uma necessidade, diante de um mercado iniciante mas promissor. O Brasil tem avançado muito em pesquisas na área de materiais e alguns produtos em desenvolvimento tais como imãs permanentes e catalisadores, requerem a utilização de alguns desses elementos com alto grau de pureza, que têm sido importados para suprimento da demanda. A exemplo disto, pode-se citar o projeto de fabricação de imãs permanentes, que vem sendo desenvolvido pelas Indústrias Nucleares do Brasil S/A (INB), em conjunto com o Instituto de Pesquisa Tecnológica (IPT) e o Instituto de Pesquisas Energéticas e Nucleares (IPEN) com apoio do PADCT. O projeto prevê a implantação de uma usina semi piloto para fabricação de imãs permanentes. A produção dos imãs prevê a utilização de samário e neodímio, ainda não produzidos comercialmente no país.

A comercialização das terras raras na forma de cloreto misto foi praticada no Brasil durante vários anos, a baixo custo, pela Nuclemon. A INB, sucessora da Nuclemon, interrompeu esta produção, com a proposta de comercializar os óxidos individuais. Para isto, a INB fez grandes investimentos e já consegue separar grande parte desses óxidos em nível de laboratório, permanecendo porém o problema de separação para muitos elementos, dentre eles, a separação dos pares praseodímio/neodímio e európio/gadolínio. O preço do cloreto misto de terras raras é da ordem de US$ 3,00/Kg e após separação das terras raras em grupo, este passa para valores em torno de US$ 9,00/Kg. O preço dos óxidos individuais de alta pureza está apresentado na tabela I.1, com destaque para os óxidos dos elementos estudados no presente trabalho: La, Pr, Nd, Eu e Gd. Estes preços variam de acordo com a quantidade, pureza, grau de dificuldade de obtenção do óxido em determinada pureza e abundância relativa do elemento nos minerais de terras raras.

Tabela I.1: Valor de mercado dos óxidos de terras raras individuais.

Óxido	**Quantidade (Kg)**	**Preço (US$/Kg)**		
		Pureza (%)		
		99	99,9	99,99
La_2O_3	100	16,80	18,20	18,90
CeO_2	100	19,90	23,00	29,50
Pr_6O_{11}	5	40,36	46,50	256,00
	100	19,50	25,00	185,00
Nd_2O_3	1	-	-	148,00
	100	15,24	15,88	-
Sm_2O_3	5	120,00	149,00	-
Eu_2O_3	1	-	627,00	695,00
	20	-	488,00	532,00
Gd_2O_3	1	-	128,00	142,00
Tb_4O_7	1	-	464,00	489,00
Dy_2O_3	1	-	216,00	-
Ho_2O_3	1	-	298,00	386,00
Er_2O_3	1	-	117,00	282,00
Tm_2O_3	1	-	790,00	840,00
Yb_2O_3	1	-	212,00	262,00
Lu_2O_3	1	-	-	760,00
Y_2O_3	5	-	-	85,00
Sc_2O_3	1	-	-	940,00

Fonte: Stanford Materials Company – 15/05/2002 (http://www.stanfordmaterials.com)

1.7. OBJETIVOS E ORGANIZAÇÃO DA TESE

Os objetivos desta pesquisa foram:

- desenvolver processo de recuperação do európio visando a obtenção do Eu_2O_3 com pureza igual ou superior a 99,9 %, bem como adquirir o domínio das variáveis dos processos estudados (redução química e fotoquímica);
- avaliar a separação do par Eu(III)/Gd(III), sem a prévia redução do európio, por extração por solventes, com o objetivo de se obter uma fração mais rica em európio a ser submetida a etapa de recuperação;
- desenvolver processo de fracionamento das terras raras leves, por extração por solventes, visando a obtenção do lantânio com pureza igual ou superior a 99 %.

Esta tese apresenta-se dividida em capítulos. Após a introdução (capítulo 1) são apresentados os resultados obtidos no presente estudo, capítulos 2 a 6. Nos demais capítulos são apresentados: as considerações finais (capítulo 7), as contribuições específicas deste trabalho (capítulo 8), as sugestões para futuros trabalhos (capítulo 9) e as publicações geradas no período, relacionadas com o tema abordado neste trabalho (capítulo 10).

No capítulo 2 (publicado na revista *Hydrometallurgy*, v.49, 1998, p.167-177 – Referência bibliográfica n$^{\underline{o}}$. 30), são apresentados os resultados de um estudo abrangente dos parâmetros do processo de redução química do európio, utilizando uma solução pura de cloreto de európio. Em seguida, as condições selecionadas foram aplicadas a uma solução comercial de cloreto samário, európio e gadolínio, contendo ainda outras terras raras, como neodímio, térbio e ítrio. A concentração de terras raras totais da amostra era de 187,4 g L^{-1}, com uma relação de óxido de terras raras totais/óxido de európio de 78.

O capítulo 3 (publicado na revista *Hydrometallurgy*, v.60, 2001, p.247-253 - Referência bibliográfica n$^{\underline{o}}$. 31) pode ser considerado como uma continuação do capítulo 2. A solução comercial estudada nesse capítulo é composta apenas de európio e gadolínio, porém com uma alta concentração de gadolínio (relação Gd/Eu de 27). Foi realizado também um estudo complementar com a solução pura de cloreto de európio.

No capítulo 4 (publicado na revista *Separation Science and Technology*, v.37 (14), 2002, p.3305-3321 - Referência bibliográfica n$^{\underline{o}}$. 34), estudou-se recuperação do európio utilizando a técnica de redução fotoquímica. Com a mesma abordagem do estudo de redução química, primeiro foi feita uma avaliação das principais variáveis do processo, com uma solução pura de cloreto de európio. Em seguida, os estudos foram complementados com a solução comercial contendo a mistura de európio e gadolínio utilizada no capítulo 3.

O capítulo 5 focaliza um estudo de extração por solventes realizado com a amostra comercial contendo a mistura de európio e gadolínio. O objetivo desse estudo foi identificar as condições favoráveis para se fazer uma pré concentração de európio antes de sua recuperação pela técnica de redução.

O capítulo 6 apresenta um estudo de fracionamento de terras raras leves (La, Pr e Nd) e descreve o processo de obtenção do lantânio, de alto grau de pureza, desenvolvido neste trabalho. Inicialmente, foi realizado um estudo de bancada, onde as principais variáveis do processo foram investigadas. Em seguida, foram realizados experimentos contínuos, visando a separação do lantânio do par Pr/Nd.

No anexo 1 é apresentada uma cópia do trabalho “Obtenção de Európio de Alto Grau de Pureza” publicado nos anais do XVIII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa e I Seminário de Química de Colóides Aplicada à Tecnologia Mineral, realizado no período de 23 a 26 de agosto de 1998 em Águas de São Pedro - S.P. O anexo 2 contém o trabalho “Recuperação de Európio e Ítrio a partir de tubos de televisores em cores” apresentado no 55^{o} Congresso da ABM, no período de 24 a 28 de julho de 2000 no Rio de Janeiro, R.J.

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CAPÍTULO 2

RECOVERY OF EUROPIUM FROM A RARE EARTH CHLORIDE SOLUTION

ABSTRACT

A two-stage Jones reductor column has been applied to the separation and purification of europium from a commercial rare earth chloride solution. The process consists of the reduction of Eu(III) to Eu(II) by a zinc amalgam, followed by the precipitation of europium(II) sulphate ($EuSO_4$) in an inert atmosphere (CO_2). Variables such as acidity, concentration and flow rate of the rare earth chloride solution in the Jones column, mercury concentration in the zinc amalgam, concentration of the precipitating agent (sulphuric acid), and the inert gas flow rate, have been evaluated with a pure europium synthetic solution. Based on the results, the experimental conditions have been adjusted to recover europium from a commercial rare earth solution, containing 2.4 g L^{-1} Eu_2O_3, 114.4 g L^{-1} Sm_2O_3 and 64.2 g L^{-1} Gd_2O_3 as the main constituents. The final product, assaying 99.4% Eu_2O_3, was obtained with a recovery of 92% .

Keywords: europium reduction, europium purification, jones reductor, Rare earth separation.

2.1. INTRODUCTION

The technological development of the last decades in sectors of the electronics industry has increasingly relied upon the supply of highly purified rare earth oxides, such as Eu_2O_3. The discovery in 1964 of an europium-yttrium based red phosphor for the production of the cathode ray tube of commercial TV sets represented a major technological breakthrough and a turning point for the rare earth industry. Europium compounds are also used in X-ray screens, high-intensity mercury vapour lamps, neutron scintillators, charged-particle detectors and optically read memory systems [1,2].

The separation of the rare earth elements is usually carried out by solvent extraction. However, the similarity of Eu(III)-Gd(III) extraction coefficients hinders the direct application of this process to separate Eu from its associates, samarium and gadolinium. Europium is recovered by precipitation as insoluble $EuSO_4$ after the reduction of the trivalent species to the divalent state. Further solvent extraction stages separate and purify gadolinium and samarium [3,4]. The reduction of Eu(III) to Eu(II) has traditionally been accomplished by use of metallic zinc or zinc amalgam [3,5,6]. The advantages of zinc powders over other reducing agents are indicated in the literature by Preston and du Preez [7]. The authors compared reactive metals (Zn and Mg), metal amalgams (Zn, Na and Eu), metal hydride and nitrogenous reductors for europium reduction in pure, synthetic and commercial solutions. Both zinc or europium amalgams worked well with the mixed rare earth solutions. Europium amalgam was further discarded “owing to the inconvenience of having to divert at least one-third of the europium content of the feed liquors through the electrolytic amalgam formation step”. The final selection was a method that combined reduction with zinc amalgam, precipitation of the sulphate, and solvent extraction to remove zinc ions from the rare earth mother liquor. Other techniques, such as photochemical reduction [8,9,10], electrochemical reduction [11,12,13] have been also proposed but there is no indication that these methods are already applied on industrial scale.

The “Indústrias Nucleares Brasileiras-INB” is responsible for the total Brazilian rare earth production. In this plant, a carbonate mixture of europium and gadolinium has been produced and stockpiled for future processing. The present work is part of a broader investigation aimed at selecting a process for the production of purified rare earth oxides from the INB carbonate mixture. The work focuses on the extraction of europium from synthetic and commercial rare earth chloride solutions using Zn amalgam. The lack of information concerning europium extraction, probably by proprietary reasons, led to the experiments involving synthetic solutions. The results obtained provided the basis to establish the conditions applied to the processing of a commercial solution.

2.2. EXPERIMENTAL

2.2.1. Reagents and Solutions

Synthetic solutions were prepared with europium oxide (99.5% Eu_2O_3) supplied by Rhone-Poulenc, Inc. The oxide was dissolved in HCl with the acidity being adjusted for the conditions of the experiments.

The commercial solution, provided by the “Indústrias Nucleares Brasileiras-INB”, consisted of a sample of raffinate from the extraction cycle of the medium and heavy rare earth separation stage. In order to produce more concentrated solutions and to adjust the acidity, the rare earth elements were precipitated with sodium carbonate and the solids calcined at 800ºC to obtain the oxides. These oxides were dissolved in a small volume of concentrated (37.2%) HCl. The volume was adjusted with water to a final acidity of 0.005 mol L^{-1} and a total rare earth concentration of 187.4 g L^{-1}, with 2.4 g L^{-1} Eu_2O_3. The solution composition is shown in Table II.1.

Table II.1: Commercial feed solution composition

RE_2O_3	**Composition**	
	g.L^{-1}	**%**
La_2O_3	<0.02	<0.002
Ce_2O_3	<0.02	<0.002
Pr_6O_{11}	<0.02	<0.002
Nd_2O_3	0.81	0.07
Sm_2O_3	114.4	9.29
Eu_2O_3	2.40	0.19
Gd_2O_3	64.2	5.21
Tb_4O_7	4.10	0.33
Y_2O_3	1.45	0.12

Density: 1.232 g cm^{-3}

The reductor, known as Jones reductor, consisted of Zn amalgam prepared by stirring, for one minute, metallic zinc powder (-1.00 + 0.59 mm) in a 1 mol L^{-1} HCl solution. Following separation from the acid solution, the solids were contacted, for three minutes, with a 0.1 mol L^{-1} mercuric (II) chloride solution, added in amounts that would provide the desired Zn/Hg ratios (0.5 and 1% of Hg). Finally, the amalgam was washed with distilled water and stored in 0.001 mol L^{-1} HCl solution. This procedure is suggested by the literature [14,15]. All solutions were prepared with analytical grade reagents and distilled water.

2.2.2. Experimental Procedure

The assembled europium reduction/precipitation apparatus was comprised basically of: (i) a glass column filled with the amalgamated zinc (Jones column), (ii) a peristaltic pump to feed the rare earth solution to the column and (iii) a flat-bottom glass precipitation kettle, standing on a magnetic stirrer. The set-up is illustrated in Figure 2.1.

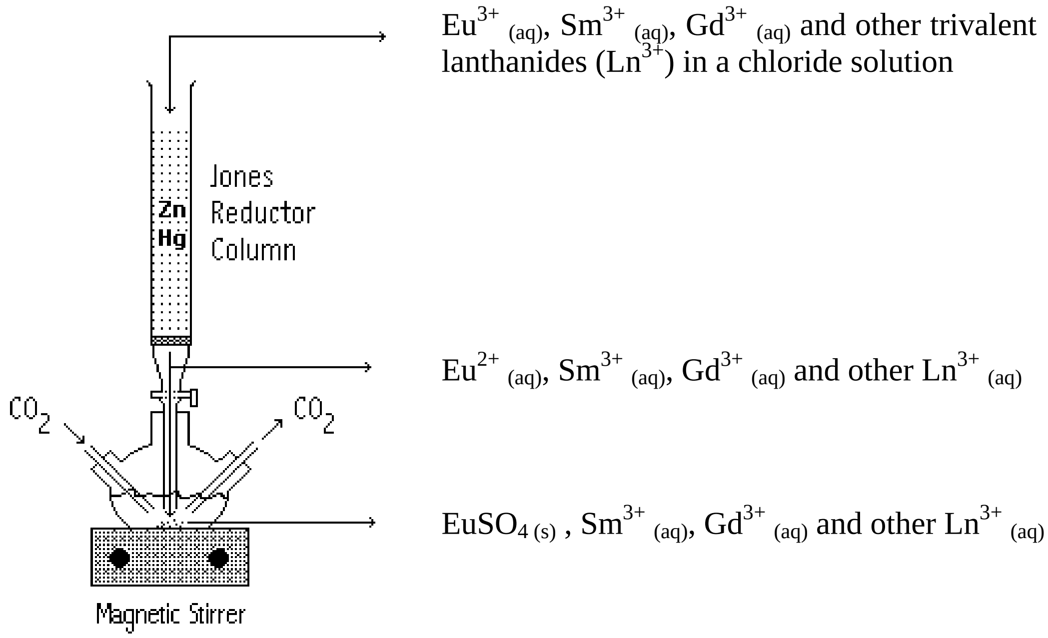

Figure 2.1. Schematic diagram of the Jones reductor.

The reduction of europium (III) was carried out in a 60 cm long and 1.6 cm wide (internal diameter) glass column, filled with 300 g of Zn amalgam (Jones reductor). The Eu_2O_3 solution (200 mL), under specified concentration and acidity, was added to the column at a flow rate of 3 mL min^{-1}. After completion, the column was washed with 80 mL of 0.001 mol L^{-1} HCl for the entire removal of europium and soluble zinc. Both the precipitation and the wash solutions were collected into the glass kettle, containing sulphuric acid solution, where the precipitation of europium (II) sulphate - $EuSO_4$ took place. The flask was maintained under CO_2 atmosphere, in order to avoid reoxidation of the reduced europium species. The solids were filtered in a Gooch-type crucible, washed with 50 mL of 0.002 mol L^{-1} ammonium sulphate solution, dissolved in HCl solution and, then, precipitated as carbonate through the addition of sodium carbonate. Finally, europium carbonate was calcined at 800°C to obtain Eu_2O_3. The recovery was calculated on the basis of europium concentration in the feed solution and in the filtrate.

These measurements were carried out by energy-dispersive X-ray spectrometry (Kevex system).

2.3. RESULTS AND DISCUSSION

The recovery of europium comprises two phenomena, namely, the reduction of Eu(III) to Eu(II) by metallic zinc, followed by precipitation of Eu(II) as europium(II) sulphate in an inert atmosphere. As a strong reducing agent, zinc is capable of reducing the hydrogen ion to H_2 as well:

$$2\ H^{+}_{(aq)} + Zn_{(s)} = Zn^{2+}_{(aq)} + H_{2(g)} \qquad Eh^{0}_{298K} = 0.76V \qquad (2.1)$$

To minimize the competition between the above reaction with the europium reduction by metallic zinc (Eq. 2.2), the metal is covered by a thin mercury layer, the resulting Zn amalgam in a column forming the Jones reductor. The Hg content in the amalgam should be kept as low as possible, since Hg does not reduce the trivalent europium species. This can be demonstrated by the reduction potential associated with Eq.(2.3) [2]:

$$2\ Eu^{3+}_{(aq)} + Zn_{(s)} = 2\ Eu^{2+}_{(aq)} + Zn^{2+}_{(aq)} \qquad \Delta E^{0}_{298K} = 0.33V \qquad (2.2)$$

$$Eu^{3+}_{(aq)} + Hg_{(l)} = Eu^{2+}_{(aq)} + Hg^{2+}_{(aq)} \qquad \Delta E^{0}_{298K} = -1.28V \qquad (2.3)$$

Europium precipitation is carried out in an inert atmosphere, since Eu(II) is easily oxidized by oxygen [6]:

$$4\ Eu^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} = 4\ Eu^{3+}_{(aq)} + 2\ H_2O_{(l)} \qquad \Delta E^{0}_{298K} = 1.66V \qquad (2.4)$$

The precipitation of Eu(II) with sulphuric acid is indicated by Eq.(2.5):

$$Eu^{2+}_{(aq)} + HSO_4^-{}_{(aq)} = EuSO_{4(s)} + H^+_{(aq)} \tag{2.5}$$

2.3.1. Synthetic Solutions

The effect of process parameters on the reduction and precipitation of europium was assessed with synthetic solutions. The investigated parameters were: HCl acidity, concentration and flow rate of the feed solution, concentration and relative amount of the precipitating agent (H_2SO_4), flow rate of the inert gas (CO_2), ageing time of the precipitate, and mercury concentration in the amalgam. Zinc dissolution (measured as Zn^{2+} in the aqueous phase) during europium reduction, and europium dissolution during washing of the $EuSO_4$ precipitate have been also investigated. Replicates prepared for randomly chosen experiments indicated an experimental error within 3 %.

Unless otherwise stated in the figure the experimental conditions were fixed at a feed flow rate of 3 mL min^{-1}, 2.5 g L^{-1} of Eu_2O_3, pH 2.5, 1% Hg in the amalgam, 30 mL of 2 mol L^{-1} H_2SO_4 (in the precipitation vessel), CO_2 flow rate of 120 mL min^{-1}, 3h ageing time.

The europium recovery was essentially independent of the feed flow rate in the range of 1 to 5 mL min^{-1}. For flow rates varying from 1 to 5 mL min^{-1}, the difference in europium recovery was only 5 %. In the subsequent experiments, the flow rate was kept at 3 mL min^{-1}. Higher flow rates did not remain stable for long periods of time. The selection of an adequate flow rate is determined by the column characteristics and the europium concentration in the feed solution. Cooley and Yost [16], using a similar apparatus, applied a flow rate of 2 mL min^{-1}. McCoy [5] and Hillebrand et al.[15] studied flow rates up to 30 mL min^{-1}.

The feed solution concentration was varied from 0.50 g L^{-1} to 5.0 g L^{-1} of Eu_2O_3. Recovery increased with the increase of europium concentration (Figure 2.2). Despite of the feed conditions, europium concentration in the aqueous phase (filtrate) remained constant in the level of 0.10 g L^{-1} of Eu_2O_3. Murthy [17] and Krumholtz [18], added barium chloride to the feed solution in order to form $BaSO_4$ seeds, thus favouring $EuSO_4$ precipitation. In the present work, addition of barium chloride did not reduce the europium concentration in the filtrate.

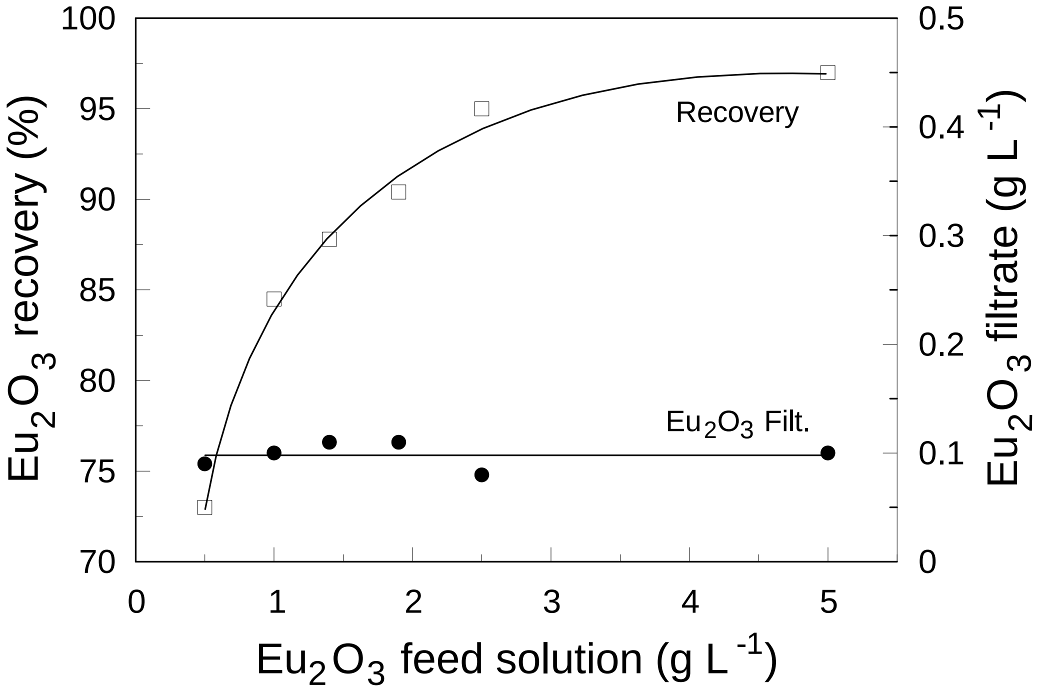

Figure 2.2. Correlation between Eu_2O_3 concentration in the feed solution and in the filtrate, with europium recovery (synthetic solution).

Acidity was studied from 0.001 to 0.100 mol L^{-1} HCl. This parameter directly affects europium reduction and the stability of the Jones reductor as well. This may be explained by the competition between europium and hydrogen reduction reactions (Eqs. (2.1) and (2.2)), and zinc dissolution. The increase of acidity may be compensated by the increase in the Hg content in the amalgam. However, a higher mercury content will decrease the process efficiency, since Hg does not participate in the reduction reaction. The experimental results indicated that an acidity below 0.003 mol L^{-1} HCl minimizes the consumption of zinc in the reductor, without affecting europium recovery

(Figure 2.3). Values below 0.001 mol L^{-1} HCl have not been tested, due to the low Eu_2O_3 solubility at pH> 3.

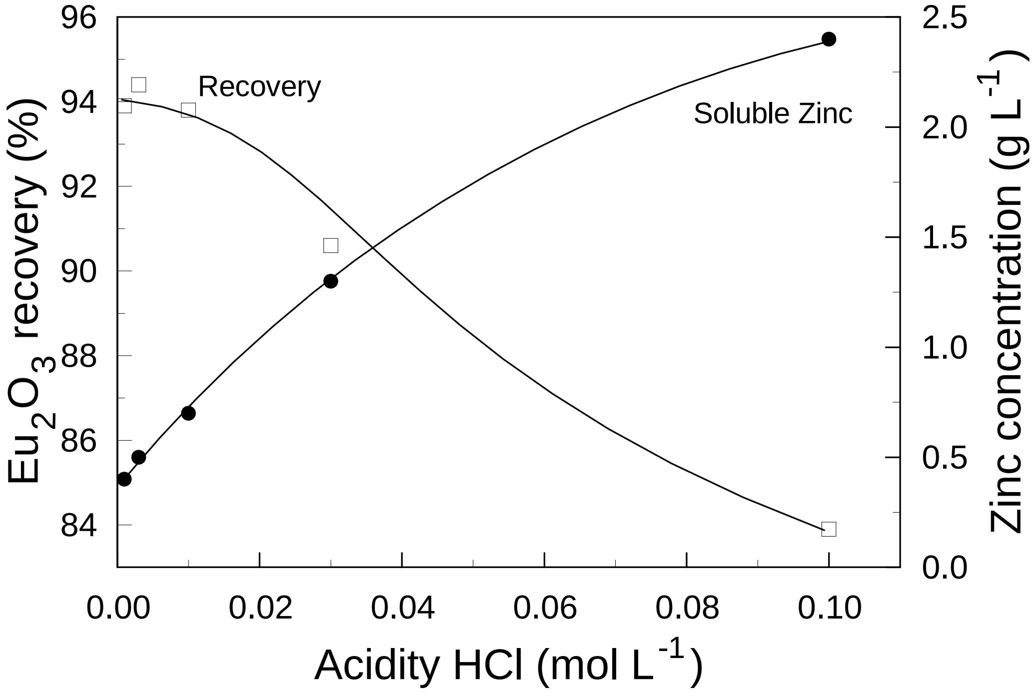

Figure 2.3. Influence of feed solution acidity on $EuSO_4$ recovery and on zinc dissolution (synthetic solution).

Stone [14] suggests 0.1% to 10% Hg concentration in the amalgam. The ideal amalgam is one that allows a quick and full Eu(III) reduction, with the minimum possible H_2 liberation. Therefore, in choosing the Hg content in the amalgam, attention must be paid to the oxidant nature and to the acidity of the feed solution. Higher Hg concentrations may be used for oxidants which are reduced by both Zn and Hg. High Hg concentration is also recommended for feed solutions with high acidity level, so as to decrease H_2 formation. If, however, Hg is not part of the reduction reaction, high Hg concentrations will reduce the column efficiency. This being the case with europium (see Eqs. (2.2) and (2.3)), lower Hg concentrations are recommended. The variation from 0.5 % to 1 % Hg concentration in the amalgam had no significant effect on europium recovery, under the experimental conditions chosen for the present work.

Eu(II) is easily oxidized by the air, as indicated by Eq. (2.4). This oxidation can be avoided by maintaining an inert gas atmosphere in the vessel where the precipitation takes place. According to McCoy [5,6], even in a CO_2 atmosphere, approximately 1% of Eu(II) is oxidized back to Eu(III). The CO_2 flow rate was studied in the range from 25 to 300 mL min^{-1}. In this range the flow rate had no significant effect on europium recovery.

The sulphuric acid concentration in the precipitation vessel was varied from 0.25 to 5 mol L^{-1}. The volume was set at 30 mL, the minimum to cover the feed solution inlet and the CO_2 tubes. Based on the reaction stoichiometry, 0.0028 mol of H_2SO_4 is needed to precipitate the 0.5 g of Eu_2O_3 fed to the system. This corresponds to a concentration of 0.0933 mol L^{-1} of H_2SO_4 in a total 30 mL volume. Therefore, a concentration of 0.25 mol L^{-1} already corresponds to an excess of 200%. The sulphuric acid concentration was increased up to 5 mol L^{-1} as an attempt to shift reaction(5) to the right, thus increasing europium recovery. Figure 2.4a indicates that recovery slightly increases with H_2SO_4 concentrations higher than 2.0 mol L^{-1}. Three hours were required to obtain a clear solution, free of suspended solids. Longer ageing times did not improve the results.

2.3.2. Commercial Solution

The results obtained with the synthetic solutions indicated europium concentration in the feed, and the concentration of sulphuric acid in the precipitation vessel as the major parameters affecting europium recovery. Exploratory tests with the commercial solution have confirmed that other parameters, such as feed and CO_2 flow rates, do not affect europium recovery. The dilute raffinate solution provided by INB for the present investigation, required prior concentration in order to increase recovery. Nevertheless, europium content was limited to a maximum of 2.4 g L^{-1} Eu_2O_3 by the corresponding high total rare earth concentration (187.4 g L^{-1}) in the feed (Table II.1). Attempts to further increase europium concentration was found to be detrimental to the complete solubilization of the oxides at the selected HCl acidity.

The results obtained with synthetic solutions indicated that recovery is nearly independent of acid concentrations higher than 2 mol L^{-1} H_2SO_4 (Figure 2.4a). Conversely, Figure 2.4b shows that both recovery and grades are significantly affected by sulphate concentration in the precipitation vessel. Experiments carried out with 30 or 60 mL of the H_2SO_4 solution, under conditions of constant H_2SO_4/europium ratio in the precipitation vessel, led to similar results. At 2.0 mol L^{-1} H_2SO_4. recoveries were 95% and 60%, respectively, for the synthetic and the commercial solutions. For the latter, a maximum europium recovery of 92% was attained with the increase of acid concentration up to 3.5 mol L^{-1} H_2SO_4; the increase compensated for the presence of samarium and gadolinium in the feed solution. In the purification stage, which involved the processing of solutions containing low concentrations of Sm and Gd, the effect of sulphuric acid concentration on europium recovery was similar to that depicted by the synthetic solution.

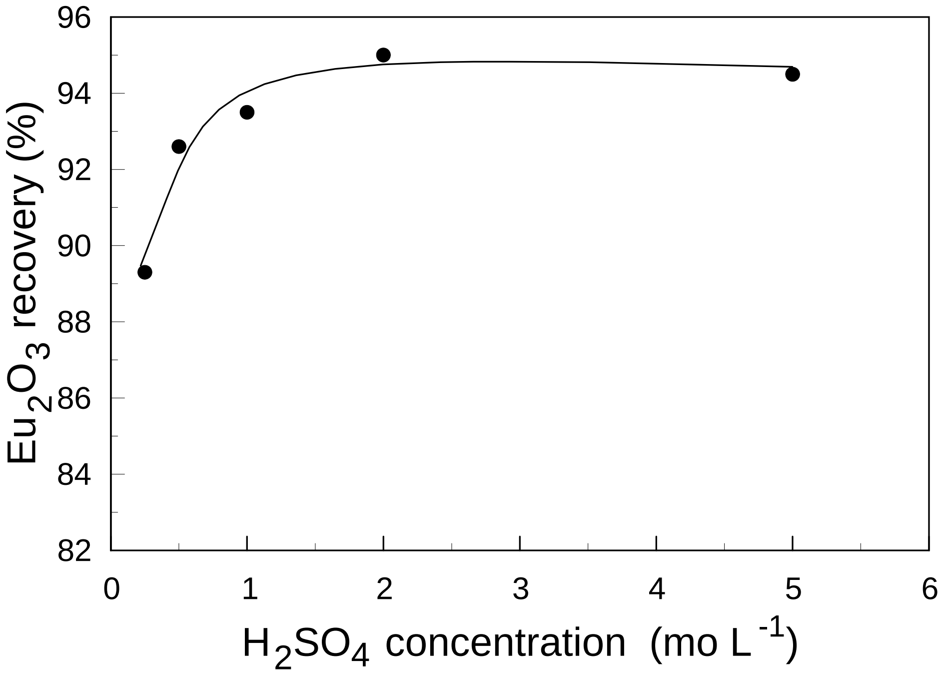

Figure 2.4a. Influence of H_2SO_4 concentration on europium recovery (synthetic solution).

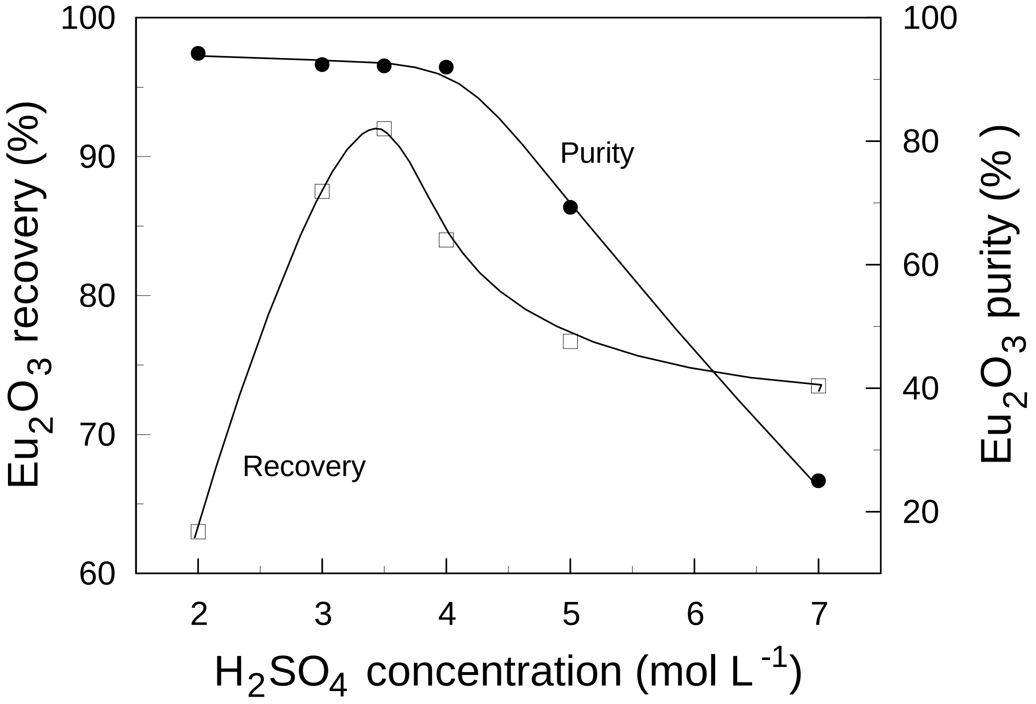

Figure 2 4b. Influence of H_2SO_4 concentration on europium recovery and purity (commercial solution - first stage) - 2.4 g L^{-1} of Eu_2O_3, pH 2.3.

Cooley and Yost [16] utilised 50 mL of a 8.0 mol L^{-1} H_2SO_4 solution to precipitate 0.7 g of Eu_2O_3, corresponding to an excess superior to 7000%. In the present work, concentrations superior to 3.5 mol L^{-1} H_2SO_4 were shown to be inadequate, due to the high samarium and gadolinium concentrations in the commercial solution. High sulphate concentrations caused the precipitation of these elements, thus decreasing both purity and recovery (Figure 2.4b). The product compositions at 5 mol L^{-1} H_2SO_4 (69.3% Eu_2O_3, 22.2% Sm_2O_3, 8.1% Gd_2O_3, 0.4% Nd_2O_3) and at 3.5 mol L^{-1} H_2SO_4 (92.2% Eu_2O_3, 6.6% Sm_2O_3, 0.9% Gd_2O_3, 0.3% Nd_2O_3) corroborates that hypothesis. Preston and du Preez [7] also correlated with coprecipitation, the decrease of europium recovery from a middle rare earth strip liquors compared with the recoveries obtained with pure europium solutions.

Many repetitions of the reduction/precipitation procedure are likely to be necessary to achieve the specification (99.99% Eu_2O_3) required for red phosphor manufacture. In the present investigation, the separation was limited to two stages. In the first one an intermediary product was obtained. The experimental conditions were set at: feed flow rate of 3 mL min^{-1} containing 2.4 g L^{-1} Eu_2O_3; pH 2.3; 120 mL min^{-1} of CO_2; 1% of Hg in the Jones reductor; 3.5 mol L^{-1} of H_2SO_4 (30 mL), ageing time of 3 h. The solids were further dissolved and reprecipitated. At this second stage (purification stage), H_2SO_4 concentration was maintained at 0.5 mol L^{-1}, Eu_2O_3 in the feed solution was 5.5 g L^{-1} and pH was 2.5. The other parameters were fixed according to those in the previous stage. The intermediary solution and final product compositions are shown in Table II.2. A product with 99.4% of Eu_2O_3 was obtained with 92% metal recovery. Higher grades can be obtained with additional purification steps, as mentioned previously, and a better separation of the heavy and light rare earth metals at the solvent extraction stage.

Table II.2: Characterization of the intermediary solution and final solid product

	SAMPLE	
RE_2O_3	**Intermediary solution ($g.L^{-1}$)**	**Final solid product (%)**
La_2O_3	< 0.02	0.03
Ce_2O_3	< 0.02	0.02
Pr_6O_{11}	< 0.02	0.01
Nd_2O_3	0.02	0.04
Sm_2O_3	0.40	0.40
Eu_2O_3	5.50	99.4
Gd_2O_3	0.06	0.03
Tb_4O_7	< 0.02	< 0.03
Y_2O_3	< 0.02	< 0.03

Despite the good results obtained with zinc amalgam by the present and other recent investigations [7], the toxicity of mercury is certainly a matter of concern and it will affect the operating costs of an industrial operation. Closed systems and careful control are required. It does not necessary imply that the method should not be considered for new plants. The production of europium occurs in a scale that facilitates this operation control. Nevertheless, the application of other reducing techniques is currently under investigation. The final selection will take into account recoveries and environmental aspects as well.

2.4. CONCLUSIONS

Europium recovery was shown to be mainly affected by the initial metal concentration in the aqueous phase and acidity. Dilute solutions required prior concentration in order to increase recovery. Recovery decreased as acidity increased, due to the formation of H_2. The sulphuric acid concentration played an important role during the precipitation of the sulphate salt from a multi-component solution. Increasing concentration lead to coprecipitation, that lowered recovery and grades. A product assaying 99.4% Eu_2O_3 was obtained from a solution containing 2.40 g L^{-1} of europium oxide; metal recovery was 92%.

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CAPÍTULO 3

RECOVERY OF EUROPIUM BY CHEMICAL REDUCTION OF A COMMERCIAL SOLUTION OF EUROPIUM AND GADOLINIUM CHLORIDES

ABSTRACT

A chemical reduction-precipitation process was applied to the separation and recovery of high-grade europium oxide from a europium/gadolinium mixture containing 1.90% Eu_2O_3. The effects on europium recovery of the presence of mercury in the reducing agent, temperature, aging time, the nature of the sulfate carrier, and the method of addition of the precipitation agent were studied in detail. Similar grades (95.0 ± 0.5% Eu_2O_3) were obtained with both Zn amalgam and pure Zn powders. The precipitation with sulfuric acid was more selective as compared to that with ammonium sulfate (95% and 80% Eu_2O_3, respectively, for 95% recovery). The continuous addition of the precipitating agent was the main factor responsible for improving europium grades, which increased from 93 to 97% in the first stage, with less acid requirements (SO_4^{2-} : Eu molar ratio decreased from 16 to 5.3). After two stages of reduction-precipitation, grades were higher than 99.99% Eu_2O_3 and recovery was 94%. The levels of individual rare earth impurities in the final Eu_2O_3 product were below 0.001%.

Keywords: europium, chemical reduction, gadolinium

3.1. INTRODUCTION

Over the last decades, the need for highly purified rare earth oxides has increased as applications expand and diversify. High grade (99.99%) europium oxide has important uses as red phosphor in color television screens and in computer monitors, compact fluorescent light bulbs, X-ray and tomography scans [1,2]. Europium is one of the least abundant of the rare earth elements, accounting for only 0.05-0.10% of the total rare earth content in its ores. Generally, the separation of this element begins with the digestion of the ore with H_2SO_4 or NaOH and further precipitation as a mixture of rare earth hydroxides [3]. These precipitates are then leached with HCl solution and submitted to liquid-liquid separation with extractants such as the di(2-ethylhexyl phosphoric acid) - DEHPA to obtain the light (La, Ce, Pr, Nd), the middle (Sm, Eu, Gd), and the heavy (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) rare earth fractions [4,5].

The likeness of Eu(III) and Gd(III) extraction coefficients hinders the direct application of solvent extraction to further isolate these elements; the separation relies upon the redox characteristics of europium. The rare earth elements are inherently present as trivalent ions in aqueous solutions, some of which can be reduced to divalent ions: Sm, Eu, Tm and Yb. Among these, Eu(III) has the highest standard redox potential, which makes possible its selective reduction and recovery from a mixture containing the other trivalent rare earth ions [6]. This reaction can be accomplished by several techniques, such as chemical reduction by Zn or Zn-Hg [1,7,8], photochemical reduction [9-11] and electrochemical reduction [12-14]. The recovery is finally accomplished by precipitation with sulfate, based on the fact that the chemical properties of Eu(II) are similar to those of the alkaline earth ions [15].

Although the separation of rare earth elements into the light, medium and heavy groups is widely known, the production of the individual elements to meet the requirements for industrial applications has not been disclosed. In the plant responsible for the total Brazilian rare earth production, a carbonate mixture of europium and gadolinium has been produced and stockpiled for future processing. This investigation focuses on the extraction of europium using a chemical reduction - precipitation process, as part of a project aimed at selecting a process to produce the purified rare earth oxides. In a previous study [16], process variables such as acidity, concentration and flow rate of the rare earth chloride solution, mercury concentration in the zinc amalgam, concentration of the precipitating agent, and the inert gas flow rate were evaluated. In that work, purity was no higher than 99.4% Eu_2O_3, this value being too low for the more noble applications. As an attempt to improve recovery and to obtain the desired purity in less reduction/precipitation stages, samarium was then removed by solvent extraction, using DEHPA as extractant. Working now with a Eu-Gd mixture, the study is complemented by comparing the reduction by pure metallic zinc and zinc amalgam, and with different sulfate sources, like $(NH_4)_2SO_4$, K_2SO_4, Na_2SO_4, $NaHSO_4$ and H_2SO_4, used as precipitating agents. The effects of temperature and aging of the precipitate on europium recovery were evaluated as well. Finally, the addition rate of the selected sulfate source, which in turn affects supersaturation, was also investigated in detail. By improving process conditions, a remarkable increase in the purity of the Eu_2O_3 product was obtained and is reported here.

3.2. EXPERIMENTAL

3.2.1. Reagents and Solutions

Pure Eu(III) solutions were prepared from europium oxide (99.5 %wt. Eu_2O_3 supplied by Rhone-Poulenc) dissolved in concentrated hydrochloric acid. The resulting solution was diluted to 2.5 g L^{-1} Eu_2O_3 with adjustment of acidity to 0.003 mol L^{-1}. The commercial solution was prepared from a europium and gadolinium carbonate mixture (1.90 %wt. Eu_2O_3 and 52.9 %wt. Gd_2O_3) supplied by “INB - Industrias Nucleares do Brasil S.A.”; the chemical composition is shown on Table III.1. The carbonate was dissolved in an aqueous HCl solution (3 mol L^{-1}) and the Eu_2O_3 and Gd_2O_3 concentrations were 5.0 and 138.2 g L^{-1}, respectively, with 0.003 mol L^{-1} of acidity.

Table III.1: Chemical composition of the europium and gadolinium carbonate mixture

Species	**Sm^{3+}**	**Eu^{3+}**	**Gd^{3+}**	**Tb^{3+}**	**CO_3^{2-}**	**Cl^-**	**Fe^{3+}**	**H_2O**
Content (wt.%)	<0.005	1.64	45.42	<0.005	43.30	2.30	0.06	7.28

The zinc amalgam (1 %wt. Hg) was prepared from metallic zinc powder (99.98 %wt.), with particle sizes in the 0.59 - 1.00 mm range. Zinc powder was first stirred in a 1.0 mol L^{-1} HCl solution, for 1 min, and then contacted for 3 min with a 0.1 mol L^{-1} mercuric chloride solution ($HgCl_2$). The volume of $HgCl_2$ solution added depends on the zinc amount, e.g. for 100 g of Zn, 50 mL of solution is necessary. Finally, the amalgam was washed with distilled water and stored in a 0.001 mol L^{-1} HCl solution. All solutions were prepared with analytical grade reagents and distilled water.

3.2.2. Reduction and Precipitation Experiments

The assembled europium reduction/precipitation apparatus was described in detail in a previous publication [16]. The reduction reaction was carried out in a glass column, 60 cm long and 1.6 cm wide (internal diameter), containing 300 g of the reducing agent (Zn or Zn-Hg). The precipitation reaction was carried out in a flat-bottom glass precipitation kettle, with four entrances. In this work, the magnetic stirrer was replaced by a mechanical agitation device in order to improve the stirring system. The feed solution was added to the column by a peristaltic pump at a flow rate of 3 mL min^{-1}. The volume of pure europium solution was 200 mL, while the volumes of the commercial solution were 200, 500 and 1000 mL. After that, the column was washed with 80 mL of HCl (0.001 mol L^{-1}) to remove all europium and soluble zinc. The feed and washing solutions were collected into the glass kettle, containing the sulfate solution for the $EuSO_4$ precipitation. The flask was maintained under CO_2 atmosphere, in order to avoid the re-oxidation of the divalent europium species.

For the commercial solution, two processes were employed. First, the sulfate solution was introduced into the flask before the reduction reaction took place. In the second process, a small amount (just to cover the feed solution inlet and the CO_2 tubes) of dilute sulfate solution (0.1 mol L^{-1} H_2SO_4) was introduced in the beginning. The remaining sulfate was added by a peristaltic pump at a flow rate of 1 mL min^{-1} during the addition of the europium solution and the precipitation continued for 2 hours under stirring. The solids were then filtered in a Gooch-type crucible and washed with 50 mL of a $(NH_4)_2SO_4$ (0.002 mol L^{-1}) solution. The $EuSO_4$ was dissolved in an HCl solution (6 mol L^{-1}) with drops of hydrogen peroxide (H_2O_2), followed by precipitation as europium carbonate through the addition of sodium carbonate. Finally, the product was calcined at 800^{o}C in order to obtain the oxide. Europium and gadolinium concentrations were measured by energy-dispersive X-ray spectrometry (Kevex system), while the control of the soluble zinc was made by atomic absorption spectrometry. Replications prepared from randomly chosen experiments indicated an experimental error within 3%, at 95% of confidence level.

The Kevex system has a radioactive source of americium (Am^{241}) with 100 mCi of activity for the X-ray generation. The complete setup is built around a Si(Li) detector X-ray spectrometer, with an energy resolution of 220 eV at 5.94 keV. The peaks observed in the X-ray fluorescence spectra are fitted with a multicomponent spectrum analysis and the intensities of the characteristic X-ray lines are extracted, for calculating the elemental concentrations. Analytical sensitivities of the order of a few μg/g can be obtained for elements with atomic numbers (Z) in the range of $40 \leq Z \leq 68$ [17-20]. The analytical sensitivity was shown to depend on the counting time. In the present work, it was adjusted to overnight counting (15 hours) for the impurity detection in the final product, and to 400 seconds for the conventional analyses. The good performance of this method was shown in solid and liquid samples.

3.3. RESULTS AND DISCUSSION

A detailed study with a pure europium chloride solution and a commercial solution was previously conducted by our group of investigation [16]. In that paper, the effects of the process parameters, such as acidity, concentration and flow rate of the feed solution, concentration of the precipitating agent, flow rate of the inert gas, aging time of the precipitate, and mercury concentration in the amalgam were described. It was observed that the feed flow rate (1 to 5 mL min^{-1}), the Hg concentration in the amalgam (0.5 to 1 %wt.) and the CO_2 flow rate (50 to 300 mL min^{-1}) did not have a significant effect on europium recovery at these levels. The acidity and concentration of the feed solution, as well as the molar ratio of SO_4^{2-} : Eu were the variables that affected europium recovery the most. This increased when the feed solution concentration or the sulfate amount in the precipitation vessel increased and when the feed solution acidity decreased. Based on europium recovery and grade, the best experimental conditions to be applied to the processing of commercial solutions were selected as follows: feed flow rate of 3 mL min^{-1}, 2.5 g L^{-1} of Eu_2O_3, pH 2.5, 1 %wt. Hg in the amalgam, CO_2 flow rate of 120 mL min^{-1}, 3 hours of aging time and SO_4^{2-} : Eu molar ratio of 38. A final product, assaying 99.4% Eu_2O_3, was obtained [16]; this grade is still inadequate for red phosphor applications. Now, the effects of the presence of mercury in the reducing agent, temperature (20 to 50°C), aging time (1 to 5h), the nature of the sulfate carrier ($(NH_4)_2SO_4$, K_2SO_4, Na_2SO_4, $NaHSO_4$, H_2SO_4) on europium recovery and the rate of addition of the selected precipitation agent were studied in detail.

The overall process, involving the reduction and precipitation of europium, can be described by the following reactions:

$$2\,Eu^{3+}_{(aq)} + Zn_{(s)} = 2\,Eu^{2+}_{(aq)} + Zn^{2+}_{(aq)} \qquad \Delta E^0_{298K} = 0.33V \qquad (3.1)$$

$$Eu^{2+}_{(aq)} + HSO^-_{4\,(aq)} = EuSO_{4(s)} + H^+ \qquad \text{for pH<1.9} \qquad (3.2)$$

$$Eu^{2+}_{(aq)} + SO^{2-}_{4\,(aq)} = EuSO_{4(s)} \qquad \text{for pH>1.9} \qquad (3.3)$$

The precipitation is carried out in an inert atmosphere, to avoid the re-oxidation of europium(II):

$$4Eu^{2+}_{(aq)} + O_{2(g)} = 4H^+_{(aq)} = 4Eu^{3+}_{(aq)} + 2H_2O_{(l)} \qquad \Delta E^0_{298K} = 1.66V \qquad (3.4)$$

An undesirable parallel reaction is the formation of hydrogen gas:

$$2H^{+}_{(aq)} + Zn_{(s)} = Zn^{2+}_{(aq)} + H_{2(g)} \qquad \Delta E^{0}_{298K} = 0.76V \qquad (3.5)$$

To minimize the competition between this reaction with the europium reduction reaction (Eq.(3.1)), zinc is usually covered by a thin layer of mercury. The rate of hydrogen evolution on mercury is rather slow owing to a very high negative overpotential in aqueous solutions [21].

Various reducing agents have been investigated by Preston and du Preez [1], such as reactive metals (Zn and Mg), metal amalgams (Zn-Hg, Na-Hg and Eu-Hg), nitrogenous reducing agents (N_2H_2 and NH_2OH), and metal hydride ($NaBH_4$). The best results were obtained with Zn and Zn-Hg. Further application of pure zinc has been hindered by the physical difficulty of separating the unreacted excess of zinc powder from the europium(II) sulfate product. Differently from the apparatus used by the authors, involving the stirring of the reducing agent with the europium/sulfate solutions, in the present work it was proposed to isolate the reduction and precipitation reactions into two different vessels. Europium (III) reduction occurred in a glass column, the sulfate being precipitated afterwards. Thus, the problems to separate the unreacted excess zinc powder from the products, as reported by Preston and du Preez [1], was overcome. The zinc ions introduced into the liquor containing gadolinium are more strongly extracted by the organophosphorus acids in comparison with the lanthanides. Zinc can be removed by solvent extraction with Cyanex 925 without loss of rare earth values [1].

In our previous work [16], Hg concentration in the amalgam was investigated from 0.5 to 1 %wt. and no differences on europium recovery and purity were observed. In the present work, europium reduction with pure zinc was investigated. The overall europium recovery was not improved by the use of the amalgam: a value of 95.5% was obtained with pure Zn, whereas 94.5% was obtained with the amalgam. In these experiments, the concentration of soluble Zn found in solution after europium reduction by both amalgam and pure Zn were identical (0.37 ± 0.04 g L^{-1}). This result is explained by the low acidity of the feed solution, which determines the final pH in the reduction column and, therefore, zinc solubility [16]. When pure zinc was used, hydrogen evolution was found to increase, as expected, and a dark layer was formed on the zinc surface, reducing its efficiency after a number of cycles. This layer was identified by X-ray diffraction as a mixture of ZnO and $Zn(OH)_2$ (ICDD files 36-1481 and 38-385, respectively). The increase of temperature from 20 to 50°C was found not to improve either the grade or the recovery of the europium oxide.

The results obtained with the various precipitating agents are presented on Table III.2. For pure europium solutions, it can be observed that recovery is not affected by the sulfate source.

Table III.2: Europium recovery as a function of the sulfate source (0.5 mol L^{-1})

Precipitating agent	**H_2SO_4**	**$(NH_4)_2SO_4$**	**K_2SO_4**	**Na_2SO_4**	**$NaHSO_4$**
Initial pH	0.2	4.8	4.4	5.3	1.0
Final pH	0.7	6.7	6.7	6.8	1.5
Eu_2O_3 recovery (%)	94.5	94.8	94.2	95.0	94.0

It is important to consider the low solubility of K_2SO_4 (approximately 0.5 mol L^{-1} at 20°C) and the high price of the bisulfate salts. Thus, the study focused on the precipitation of europium from commercial solutions with H_2SO_4 and $(NH_4)_2SO_4$. A comparison between H_2SO_4 and $(NH_4)_2SO_4$ indicated similar behavior with respect to europium recovery; however, the precipitation with sulfuric acid was more selective and led to higher grade Eu_2O_3 (Fig. 3.1). For the experiments with sulfuric acid, the recovery attained its maximum (93%) at 0.09 mol of SO_4^{2-} while the grade decreased only 5% in the full-range of H_2SO_4 concentration, this decrease being caused by gadolinium precipitation. In the presence of ammonium sulfate, grades decrease abruptly for SO_4^{2-} concentration above 0.06 mol. This can be explained by the data shown on Table III.2. The high pH depicted by the ammonium sulfate solution favors gadolinium precipitation, which is the main constituent in the solution (Table III.1). Attempts to dissolve this metal from the precipitate with HCl have failed, thus indicating that the contamination of the europium(II) sulfate with gadolinium occurs either as very fine inclusions or as a solid solution.

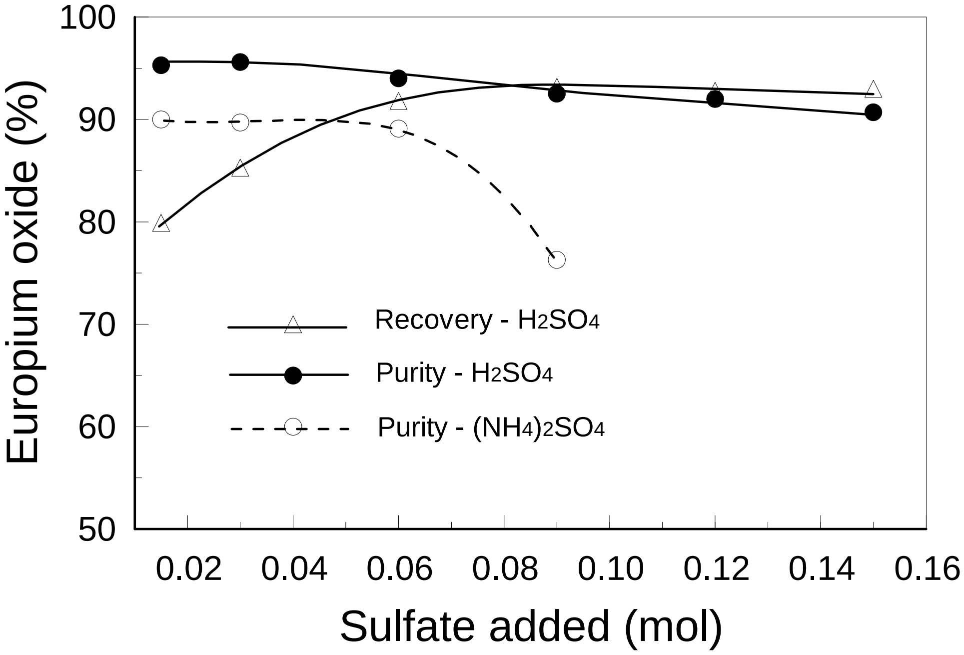

Figure 3.1. Influence of the H_2SO_4 and $(NH_4)_2SO_4$ concentration on europium recovery and purity - commercial solution.

In the present work, the effects of the H_2SO_4 concentration on europium recovery and purity were quite different from those observed in our previous investigation [16]. In that work, there was a maximum in europium recovery at 3.5 mol L^{-1} of H_2SO_4, corresponding to 0.105 moles H_2SO_4 in the system. In addition, grades decreased abruptly at 0.120 mol of H_2SO_4. In that case, the concentration of total rare earth oxides was 187.4 g L^{-1}, with 2.4 g L^{-1} Eu_2O_3. As sulfuric acid concentration increased, the other trivalent rare earth co-precipitated with europium(II) sulfate. The removal of samarium resulted in a more concentrated europium solution (5.0 g L^{-1} of Eu_2O_3) associated with a lower total amount of rare earth elements: 143.2 g L^{-1} of total rare earth oxides (Eu_2O_3 and Gd_2O_3). Therefore, this separation made it possible to double the concentration of europium in a smaller concentration of total rare earths. These differences were enough to minimize the premature trivalent rare earth precipitation, as reported before.

Another attempt to increase grade and recovery was carried out by varying the rate of addition of the sulfate source and some results are displayed in Fig. 3.2. The direct addition of H_2SO_4 was carried out by the introduction of this reagent into the precipitation flask prior to europium(III) reduction. The observed behavior was compared to the addition of a small amount (just enough to cover the feed solution inlet and the CO_2 tubes) of a diluted H_2SO_4 solution (0.1 mol L^{-1}) in the beginning, followed by its continuous addition (1.0 mol L^{-1} at a flow rate of 1 mL min^{-1}) during the europium(III) reduction reaction. Under this condition, the SO_4^{2-} concentration was maintained at lower levels during the experiment, which led to a lower supersaturation throughout the experiment as compared to the direct addition. As a result, maximum europium recovery was attained at much lower sulfuric acid amounts (molar ratio of SO_4^{2-} : Eu = 5.3, against 16 for the direct addition), while the purity increased from 93 to 97%, owing to the reduction of gadolinium coprecipitation (Fig. 3.2). In a flow rate interval from 0.3 to 1 mL min^{-1} and for a constant H_2SO_4 amount (0.045 mol), no difference on the recovery and purity of the europium oxide was observed.

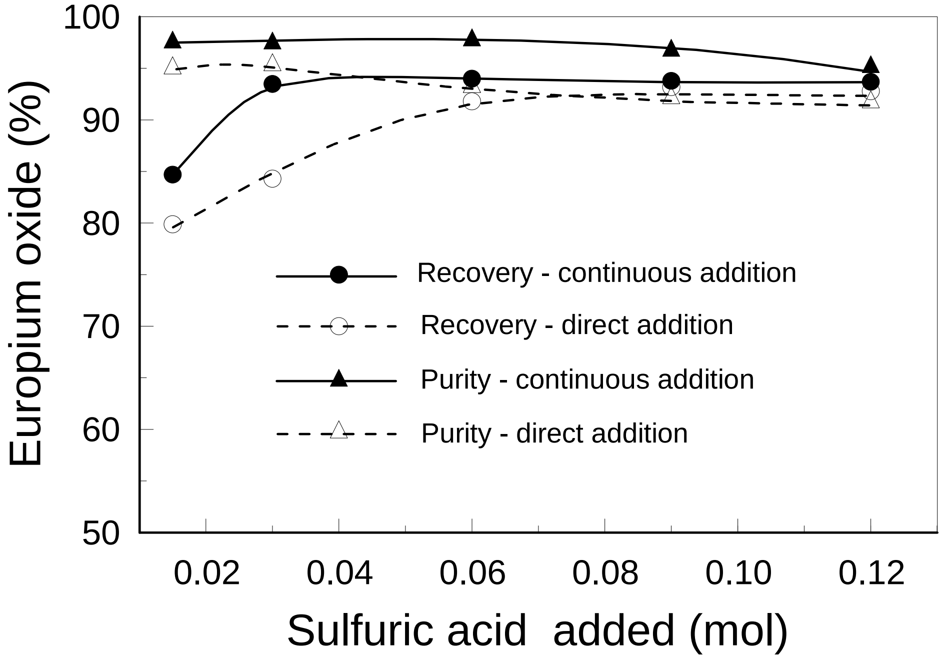

Figure 3.2. Relative influence of the direct and continuous addition of sulfuric acid on europium recovery and purity – commercial solution.

Another parameter studied was the aging time (1-5 hours). In our previous work [16], the aging time was studied in the range of 3-5 hours for the pure europium solution, 3 hours being selected as the best condition. The results of the present study indicated that this time could be reduced to two hours (Fig. 3.3). According to Preston and du Preez [1], the precipitation of europium(II) sulfate proceeds considerably more slowly in the authentic strip liquors than in pure solutions, due to the presence of impurities in this liquor, such as partially hydrolyzed iron(III) species. This was not confirmed by the present work, maybe owing to the low impurity concentration in the raw material (Table III.1).

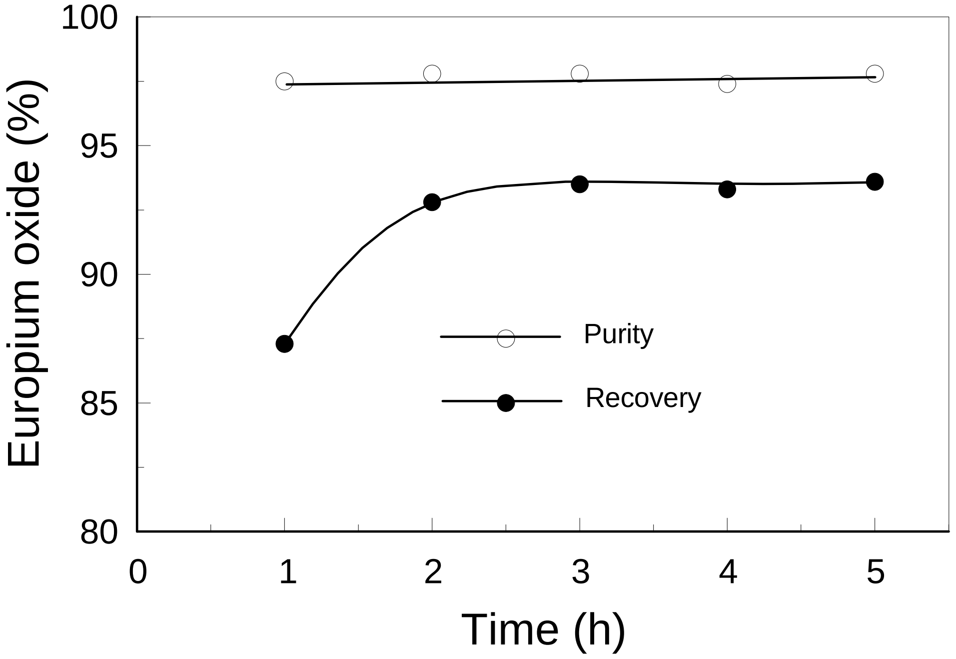

Figure 3.3. Influence of the aging time on europium recovery and purity.

With a molar ratio of Gd : Eu = 27, it was not possible to obtain a high grade europium oxide in just one stage of reduction/precipitation, and two stages were required to reach the grades needed for red phosphor manufacture. The purification, as schematically shown in Fig.3.4, was carried out under the optimal experimental conditions established in this work, such as: feed flow rate of 3 mL min^{-1} containing 5.0 g L^{-1} Eu_2O_3; pH 2.5; 100 mL min^{-1} of CO_2; Zn-Hg as the reducing agent; aging time of 2 hours; and continuous addition H_2SO_4 solution to a final molar ratio of SO_4^{2-} : Eu = 5.3. The results indicated that a product containing 99.99% Eu_2O_3 could be obtained after two stages of purification of a feed with 1.90% Eu_2O_3; the recovery was 94%.

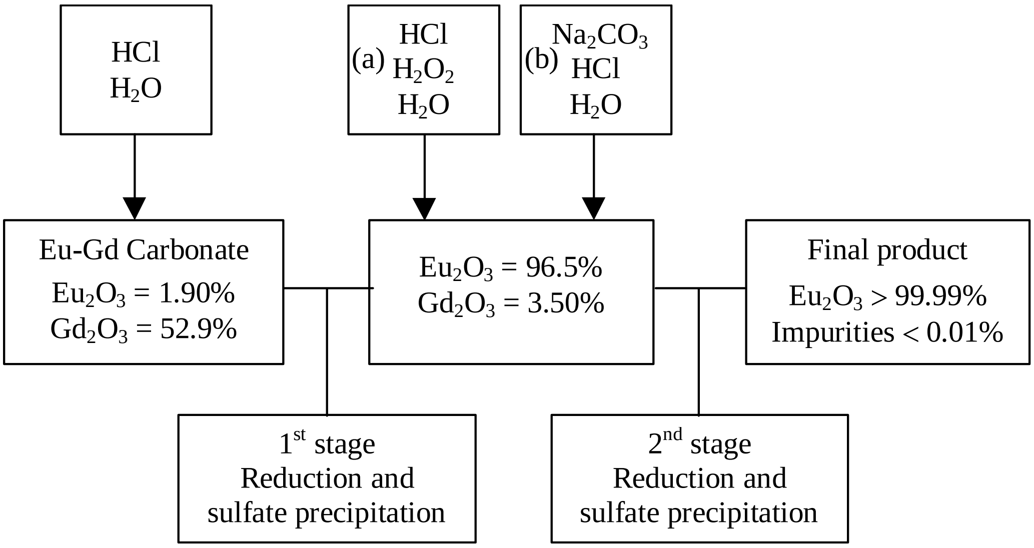

Figure 3.4. Simplified flowsheet for europium purification. (a) sulfate solubilization; (b) carbonate precipitation and solubilization.

3.4. CONCLUSIONS

Similar grade europium oxide can be produced with both Zn amalgam and pure Zn powders. The advantage of the amalgam lies on the fact that the presence of Hg hinders the formation of a zinc oxide coating, which decreases europium recovery after a number of cycles. The precipitation with sulfuric acid led to higher-grade europium oxide by keeping pH in a range that does not favor gadolinium co-precipitation. The continuous sulfuric acid addition was the main responsible for the improvement of both europium recovery and grades, with less acid requirements. Maximum recovery was achieved with an aging time of 2 hours or higher. Based on the experimental conditions established by the present study, a product assaying 99.99% Eu_2O_3 was obtained from a feed containing 5.0 g L^{-1} Eu_2O_3 and 138.2 g L^{-1} Gd_2O_3, in two stages of reduction-precipitation. The overall recovery was 94%.

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CAPÍTULO 4

EUROPIUM RECOVERY BY PHOTOCHEMICAL REDUCTION FROM Eu AND Eu-Gd CHLORIDE SOLUTIONS

ABSTRACT

The recovery of europium in aqueous chloride solution by photochemical reduction/precipitation was evaluated in the presence of sulfate ions and a radical scavenger. A commercial low-pressure mercury lamp with emission peak at 253.7 nm was used as irradiation source. The influencing factors were investigated in detail with a pure europium (III) chloride solution and then applied to a solution containing a Gd/Eu molar ratio of 27. Europium recovery was shown to increase with the increase of SO_4^{2-}/Eu molar ratio up to 7, which corresponds to a stoichiometric excess of 600%. Similarly, high scavenger requirements (Formic acid/Eu ratio of 500) were needed to achieve high yields. Faster reaction rate in the presence of formic acid, as compared with 2-propanol (2h and 15h respectively, at 99% Eu recovery), used as scavengers, was observed. This was related to the photoactivation of formic acid, demonstrated by a strong absorption in the near-UV region, not observed with 2-propanol, and a ready drop of the solution Eh. Measurements of redox potential indicated the reducing character in the formic acid system. This reducing character, that was not observed with 2-propanol, increases with the irradiation at 253.7 nm. The increase of rare earth concentration led to either Eu(III) precipitation prior to irradiation, in pure Eu solutions, or Eu-Gd coprecipitation, in multicomponent solutions. Europium recovery reached 99% when the experiments were carried out with pure, dilute europium chloride solutions. High yields could not be achieved in the presence of high gadolinium concentration, owing to Eu-Gd coprecipitation.

Keywords: europium, europium reduction, photochemical reduction

4.1. INTRODUCTION

In recent years, the interest in the commercial utilization of lanthanide compounds, such as those of europium, has significantly increased. When in high purity degree, europium oxide shows a high market value as a result of important applications, such as red phosphors in color TV tubes and computer monitors, laser materials, high-intensity mercury vapor lamps, X-ray screens, etc.

In aqueous phase, the rare earth elements are stable as trivalent species; among these elements, europium is the most easily reduced to the divalent form. Based on this feature, the separation of europium from rare earth concentrates is usually carried out by reduction of Eu(III) to Eu(II), followed by its precipitation as $EuSO_4$. The reduction can be accomplished by (i) cementation using Zn or Zn-Hg amalgam [1-5], (ii) electrochemical reduction, using titanium or graphite as cathode [6-10] or (iii) photochemical reduction, using a low-pressure mercury lamp (LPML), high-pressure mercury lamp (HPML) or excimer lasers. [11-22].

The basic differences among the sources of irradiation mentioned in the previous paragraph are the power and the region of wavelength emission. The low-pressure mercury lamp (LPML) is characterized by a lower power and higher energy photon emission, i. e. lower wavelength (for instance 184.9/253.7 nm) as compared to the high-pressure (HPML) source (310/365 nm) [14,20,21]. The excimer (a notation based on the contraction of the words *excited* and *dimer*) lasers are generally of high power and use electronic transitions between an excited and the ground state of a gas molecule. The region of emission depends on the materials composition. Most ultraviolet molecular gas lasers involve, in fact, a combination of two different atoms, frequently a noble gas and a halogen: ArF (193 nm); KrCl (222 nm); KrF (248 nm). These molecules, which are not dimers, should be called exciplex (a contraction of *excited* with *complex*) lasers [23].

The photoreduction of Eu(III) to Eu(II) takes place in the charge transfer band (CT band), corresponding to the transfer of an electron from a complexing ligand to the metal ion [17,18,24]. The reduction should be carried out in the presence of a radical scavenger to avoid the reverse reaction of oxidation. The radical scavenger, an alcohol, an ester or an organic acid, may also participate in the reduction of Eu(III), as it will be shown in this paper. The europium photoreduction can be carried out in aqueous or organic phases, the source of irradiation being dependent on the nature of the solvent. In aqueous solution, low-pressure mercury lamps or excimer lasers have been tested [18-21].

The chemical reduction of a Sm-Eu-Gd mixture was previously investigated by our group [5]. In that work, purity was no higher than 99.4% Eu_2O_3, this value being too low for more noble applications. As an attempt to improve recovery and grades in less reduction/precipitation stages, samarium was removed by solvent extraction. The combination of a more concentrated solution in europium (Gd/Eu molar ratio of 27), less concentration of total rare-earths with processing adjustments, resulted in grades higher than 99.99% Eu_2O_3, in two steps of reduction and precipitation [25]. Despite the good results, the environmental problems related to the disposal of Zn-Hg residues were a matter of concern. The photochemical reduction appears as an attractive option from the environmental point of view, since, in this case, the disposal of Hg-containing residues can be avoided. The photoreduction of europium in aqueous solutions has been previously studied in dilute, pure or equimolar mixtures (binary or ternary) of lanthanides [19-22] and, therefore, under experimental conditions that may not reflect the actual composition of industrial solutions, such as the one previously mentioned [25]. In addition, some important information, such as the influence of the redox potential, scavenger/europium and sulfate/europium molar ratios on europium recovery, is not available yet.

In the present work the photochemical reduction of europium is analyzed with the objective of europium recovery from a commercial mixture of Eu-Gd. As in the study of chemical reduction [25], discussed above, samarium was previously removed by solvent extraction. The effect of europium concentration and other variables such as nature and amount of the radical scavenger and sulfate salt, redox potential, total rare earth concentration and irradiation time have been at first evaluated in detail with a pure europium solution and then with a solution containing high gadolinium concentrations (Gd/Eu molar ratio of 27).

4.2. EXPERIMENTAL

4.2.1.Reagents

Europium chloride solutions were prepared by dissolving the oxide (99.5% Eu_2O_3 supplied by Rhone-Poulenc) in a small volume of concentrated hydrochloric acid, and these solutions were further diluted with distilled water to a final concentration of 10.0 g L^{-1} Eu_2O_3 and acidity of 0.003 mol L^{-1} (pH 2.5).

The europium/gadolinium chloride solutions were prepared by dissolving the respective carbonates (1.90% Eu_2O_3 and 52.4% Gd_2O_3) supplied by "Indústrias Nucleares do Brasil S.A. - INB" in an aqueous hydrochloric acid solution (3.0 mol L^{-1}). The concentration of Eu_2O_3 and Gd_2O_3 in the commercial stock solution was 5.0 g L^{-1} and 138.2 g L^{-1}, respectively, with 0.003 mol L^{-1} of acidity. The chemical composition of the Eu/Gd mixture is shown in Table IV.1. All other chemicals were of analytical reagent grade; distilled water was used throughout the experiments.

Table IV.1: Chemical composition of the solid europium and gadolinium carbonate mixture

Species	**Sm^{3+}**	**Eu^{3+}**	**Gd^{3+}**	**Tb^{3+}**	**CO_3^{2-}**	**Cl^-**	**Fe^{3+}**	**H_2O**
Content (%wt.)	<0.005	1.64	45.4	<0.005	43.3	2.30	0.060	7.28

4.2.2. Experimental Procedure

The europium photoreduction and precipitation were carried out in a beaker type glass bottle with 65 mm in diameter and 70 mm high, standing on a magnetic stirrer and under an ultraviolet source, at 25^oC. Two commercial low-pressure mercury lamps (LPML) of 15W (germicidal Lamp), supplied by General Electric- GE, USA, with emission peak at 253.7 nm were used as source of irradiation. The distance from the lamps to the europium solution surface was maintained at 80 mm. The solution bed was 20 mm high and the irradiation area was 33 cm^2. During irradiation, the solution temperature was observed to increase by approximately 3^oC.

The pure $EuCl_3$ stock solution (10 g L^{-1} Eu_2O_3) was diluted to the desired experimental level and the sulfate (H_2SO_4 or $(NH_4)_2SO_4$) was added to a final volume 50 mL, used in all the experiments. The radical scavengers were introduced immediately before the beginning of the experiments in order to avoid possible losses by degradation before europium reduction.

After precipitation, $EuSO_4$ was filtered in a Gooch-type crucible and washed with 0.002 mol L^{-1} ammonium sulfate solution. The precipitate was then dissolved in a HCl solution (6 mol L^{-1}) with drops of hydrogen peroxide (H_2O_2), reprecipitated as a carbonate salt through the addition of sodium carbonate and finally submitted to calcination at 800^oC to produce the oxide. The recovery was calculated by measuring europium concentration in the feed and in the filtrate solutions. The measurements were made in an energy-dispersive X-ray spectrometer (Kevex system – Kevex, CA, USA), with a detection limit of 0.01 g L^{-1}.

The Kevex system has a radioactive source of americium (Am^{241}) with 100 mCi of activity for the X-ray generation. The complete setup is built around a Si(Li) detector X-ray spectrometer, with an energy resolution of 220 eV at 5.94 keV. The peaks observed in the X-ray fluorescence spectra are fitted with a multicomponent spectrum analysis and the intensities of the characteristic X-ray lines are extracted, for calculating the elemental concentrations. Analytical sensitivities of the order of a few μg/g can be obtained for elements with atomic numbers (Z) in the range of $40 \leq Z \leq 68$ [26-28]. The analytical sensitivity was shown to depend on the counting time. In the present work, it was adjusted to 400 seconds. The good performance of this method was shown in solid and liquid samples. The experimental error including the analytical error was 3% at 95% of confidence level.

The absorption spectra of aqueous solutions of the species involved in the process were investigated using an UV-vis Perkin Elmer spectrophotometer model Lambda 20 (Perkin Elmer, USA). The redox potential was measured with a Pt electrode (Digimed pH-meter model DM 20 – Digimed, SP, Brazil) under mild stirring, using a saturated Ag-AgCl as the reference electrode.

4.3. RESULTS AND DISCUSSION

Among the lanthanides, Eu(III) is the most easily reduced to the divalent state. The photoreduction (Eq. 4.1) takes place in the charge transfer band (CT band), corresponding to the transference of an electron from a complexing ligand to the metal ion [17,18,24]. In europium (III) aqueous solution, a CT band from H_2O to Eu(III) occurs at 188 nm. In solutions containing sulfate, another CT band appears around 240 nm, corresponding to the charge-transfer transition from SO_4^{2-} to Eu(III). The hydroxyl radical ($^\bullet OH$) formed during europium reduction (Eq. 4.1) is removed by a scavenger, such as formic acid and 2-propanol, through a reaction that produces an organic radical (Eq. 4.2 e 4.3). It has been suggested that this radical may reduce a second molecule of Eu(III) ion to its divalent state [19-21]:

$$Eu^{3+}(H_2O)_n + h\nu \quad = \quad Eu^{2+}(H_2O)_{(n-1)} + {}^\bullet OH + H^+ \qquad (4.1)$$

$$HCOOH + {}^\bullet OH \quad = \quad H_2O + {}^\bullet COOH \qquad (4.2)$$

$$(CH_3)_2CHOH + {}^\bullet OH \quad = \quad H_2O + (CH_3)_2{}^\bullet COH \qquad (4.3)$$

As the Eu(II) ions are formed they are precipitated as $EuSO_4$ according to the equation:

$$Eu^{2+} + HSO_4^{-} \quad = \quad EuSO_4 + H^{+} \qquad (4.4)$$

The effect of process parameters on the reduction and precipitation of europium was first studied with pure europium solutions. Figure 4.1 compares the influence of formic acid and 2-propanol on europium reduction. It is important to emphasize that recovery of europium as $EuSO_4$ by photochemical process does not occur in the absence of the radical scavenger, which is added in order to avoid the reverse reaction (Eu(II) oxidation) [18,20-22]. As shown by Figure 4.1, relatively longer irradiation time is needed with 2-propanol, as a result of significantly slower reaction rates. In the presence of formic acid, two hours of irradiation were adequate to achieve approximately 100% europium recovery, while for the 2-propanol fifteen hours of irradiation were required to achieve comparable conversion. Similar trend was reported by Hirai and Komasawa [21], who explained their results in terms of the formation of a $^{\bullet}COOH$ radical through the photodecomposition of formic acid, this species being also capable of reducing Eu(III):

$$Eu^{3+} + {}^{\bullet}COOH \quad = \quad Eu^{2+} + CO_2 + H^{+} \qquad (4.5)$$

The authors reported that 4 hours were needed to attain equilibrium with formic acid and 24 hours with 2-propanol (irradiation wavelength at 253.7 nm). Sm-Gd coprecipitation was reported.

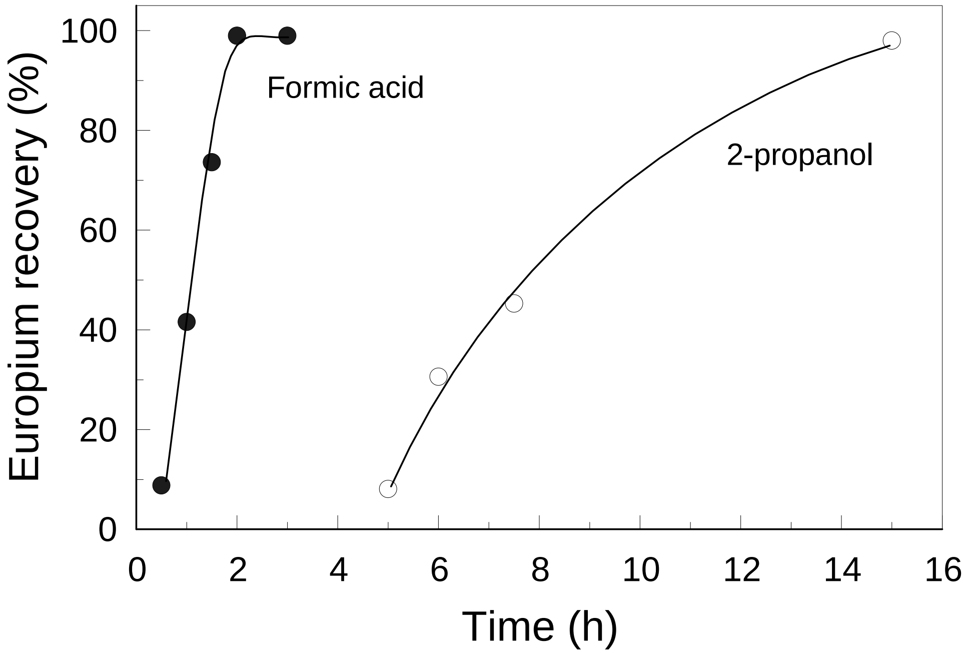

Figure 4.1. Influence of the radical scavenger on europium recovery: 7×10^{-3} mol L^{-1} Eu^{3+} (1.25g L^{-1} Eu_2O_3), molar ratios: SO_4^{2-}/Eu = 35; HCOOH/Eu = 600; $CH_3CH(OH)CH_3$/Eu = 730.

In order to investigate the differences depicted in Figure 4.1, the absorption and the redox potentials of both systems were measured. The absorption spectra of the solutions containing 2-propanol and formic acid are shown in Figure 4.2. In pure europium chloride solution (line A), only the charge-transfer band from H_2O to Eu(III) at 188 nm is observed. When SO_4^{2-} is introduced, a transition band at approximately 240 nm, corresponding to the charge-transfer from SO_4^{2-} to Eu(III) [19-21], is identified (line B). Now, the europium/sulfate system in the presence of 2-propanol and formic acid will be analyzed. The addition of 2-propanol to the solution containing $EuCl_3$ and H_2SO_4 (line C) does not modify the behavior depicted by the $EuCl_3/H_2SO_4$ solution (line B). The slightly lower absorbance level observed in the presence of 2-propanol is related to the relatively lower europium concentration caused by the addition of the scavenger. Conversely, the presence of formic acid (line D) creates a broad absorption band at around 260 nm. This band remains even in the absence of $EuCl_3$ (line E), thus indicating that the absorption is not related to an interaction (charge-transfer) involving this compound and europium. The excited electronic state of formic acid created by the absorption at 260 nm, not observed with the 2-propanol, may indirectly enhance Eu(III) reduction thus justifying the high reactivity in the presence of the formic acid, as indicated by Eqs. (4.6) to (4.8).

$$HCOOH + h\nu = {}^{\bullet}COOH + H^{\bullet} \qquad (4.6)$$

$$H^{\bullet} + H^{\bullet} = H_2 \qquad (4.7)$$

$$H^{\bullet} + {}^{\bullet}OH = H_2O \qquad (4.8)$$

Equations (4.6) and (4.7), discussed by Allmand and Reeve [29] and Hirai [21], explain the photoactivation of formic acid at 260 nm, shown in Figure 4.2. The reaction depicted by Eq. (4.6) creates an additional source of formic radical to that of the reaction of a hydroxyl radical with formic acid (Eq. 4.2), favoring europium reduction. On the other hand, it is shown by Eq. (4.8) that the formation of an $H^{\bullet}$ radical creates another pathway for scavenging the $OH^{\bullet}$ generated by Eq. (4.1), which in turn also favors Eu(III) reduction. Summarizing, the enhanced europium reduction in the presence of formic acid is related to its photoactivation, shown in Figure 4.2, which increases the reducing agent (${}^{\bullet}COOH$) concentration and provides an additional scavenger ($H^{\bullet}$) to remove the hydroxyl radical(${}^{\bullet}OH$) formed by Eq (4.1).

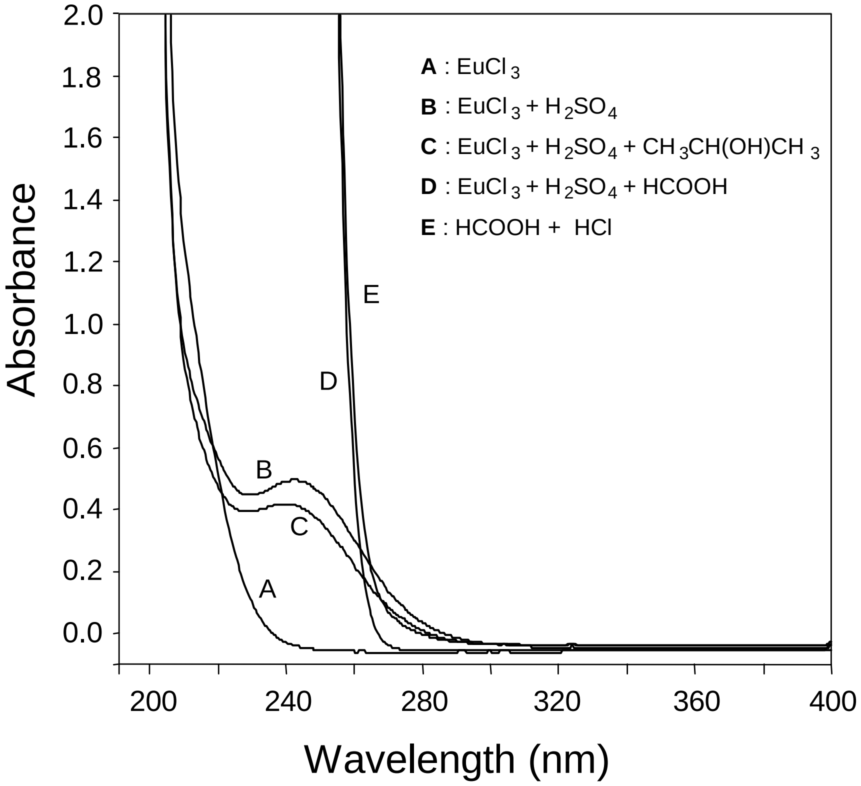

Figure 4.2. Absorption spectra of aqueous solutions (reference: air, $EuCl_3$: 0,005 mol L^{-1}, H_2SO_4: 0,25 mol L^{-1}, HCl: 0,005 mol L^{-1}, $CH_3CH(OH)CH_3$: 2 mol L^{-1}, HCOOH: 2 mol L^{-1}).

The redox potential of the aqueous solutions containing formic acid and 2-propanol was measured, before and after UV light irradiation. The potentials as a function of the irradiation time are shown in Figure 4.3. Line A represents the behavior of an aqueous europium chloride solution containing both sulfuric and formic acids. Line B represents the aqueous solution without europium (H_2O + HCl + H_2SO_4 + HCOOH) and line C is the aqueous europium chloride solution plus sulfuric acid and 2-propanol. The concentrations of the species were maintained at the experimental levels shown in Fig. 4.1 (7×10^{-3} mol L^{-1} Eu^{3+}, molar ratios: SO_4^{2-}/Eu = 35; HCOOH/Eu = 600; $CH_3CH(OH)CH_3$/Eu = 730). Before light irradiation, the potential (Eh_{298K}) was approximately 0.30 V in the presence of formic acid, while 0.55V in the 2-propanol system. The stronger reducing nature of pure formic acid solutions is magnified in the presence of the irradiation source (Fig. 4.3 - line B). In five minutes of irradiation, the potential reached an Eh_{298k} of -0.05 V in the formic acid-Eu system (line A), while more than 4 hours were needed for the potential to reach similar value with the 2-propanol-Eu solution (line C).

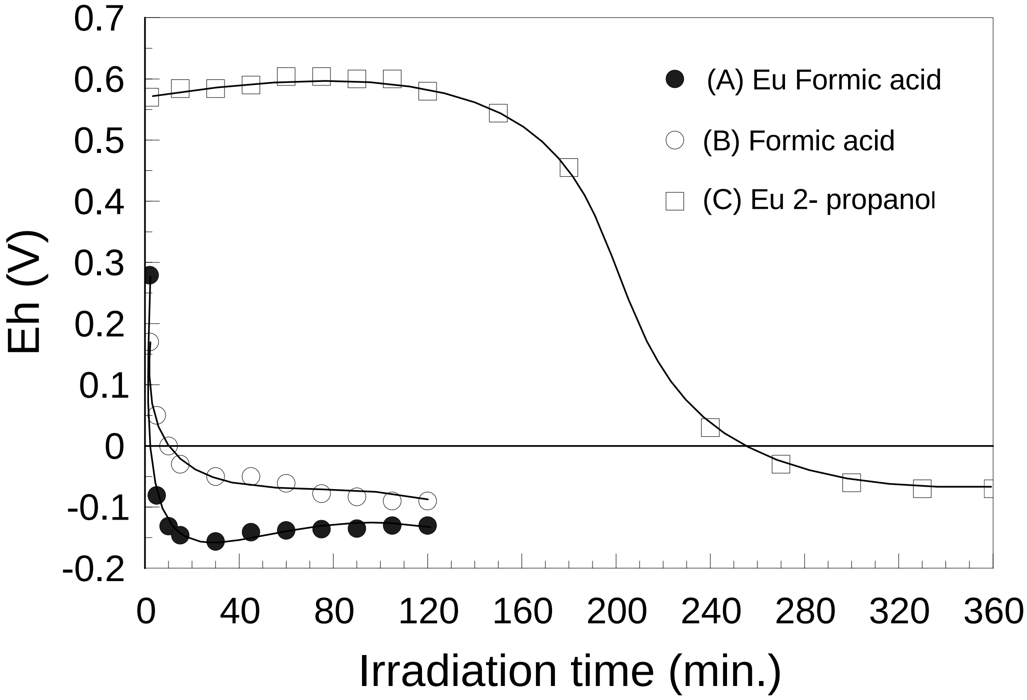

Figure 4. 3. Variation of Eh_{298K} with the irradiation time for the aqueous systems (A: $EuCl_3$, H_2SO_4, HCOOH), (B: HCl, H_2SO_4, HCOOH) and (C: $EuCl_3$, H_2SO_4, $(CH_3)_2CHOH$)

Based on its better performance, the study was continued with formic acid. The important role of the HCOOH/Eu molar ratio on europium recovery, not clearly addressed in previous studies, is depicted in Figure 4.4. The recovery increases slightly with the HCOOH/Eu ratio up to a level of approximately 500. At this point a sharp increase in recovery takes place, reaching levels of approximately 100%.

Variations of HCOOH/Eu molar ratios from 370 to 600 did not affect the redox potential; in both cases, the Eh followed the same trend depicted in Figure 4.3, stabilizing at -0.13V.

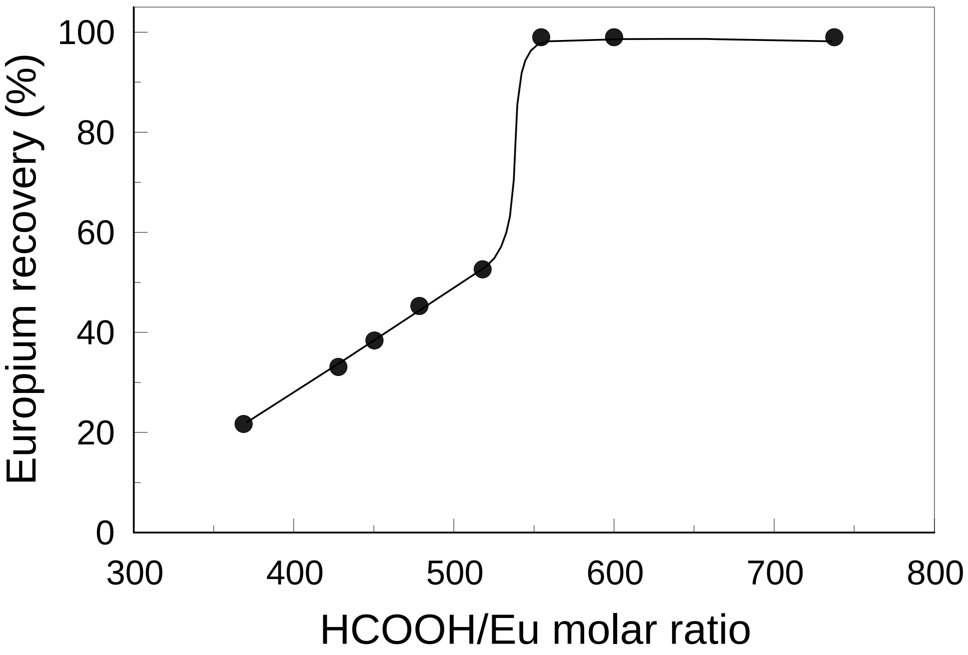

Figure 4.4. Influence of the molar ratio HCOOH/Eu on europium recovery: 8×10^{-3} mol L^{-1} (1.25g L^{-1}) Eu_2O_3, SO_4^{2-}/Eu molar ratio of 35, 2 hours of irradiation.

In the recovery of europium by photochemical reduction, sulfate ions have two important roles. The primary role of SO_4^{2-} is the removal of Eu(II) as insoluble europium(II) sulfate ($EuSO_4$), avoiding its reoxidation. In addition, the sulfate ion is also important to create a charge-transfer band around 240 nm that corresponds to the C-T from SO_4^{2-} to Eu^{3+}. This band enables the use of the commercial LPML with an emission peak of 253.7 nm. In the absence of sulfate, the absorption takes place near 190 nm, in the C-T band from H_2O to Eu^{3+} [19-21]. Nevertheless, the reduced Eu^{2+} will be photooxidized in its f-d transition, which occurs in the same wavelength of the charge-transfer transition of Eu(III) to SO_4^{2-} , the photoactivation acting as a catalyst in the oxidation reaction [12,18,21,22,30,31].

$$Eu^{2+} + H_2O + h\nu \quad = \quad Eu^{3+} + OH^- + H^\bullet \qquad (4.6)$$

$(NH_4)_2SO_4$ and H_2SO_4 were investigated as sulfate sources and led to similar europium recoveries. Sulfuric acid was selected based on the comparatively higher grade Eu_2O_3 obtained in experiments of chemical reduction of solution containing high gadolinium concentration [25]. The better results were explained by the lower pH of the medium as compared to the $(NH_4)_2SO_4$ solution, which helped to prevent gadolinium coprecipitation. The sulfate amount was then varied from SO_4^{2-}/Eu molar ratio of 1.5 to 35 (0.01 to 0.25 mol L^{-1} SO_4^{2-}). Europium recovery was shown to increase with the increase of SO_4^{2-}/Eu molar ratio up to 7, which corresponds to a stoichiometric excess of 600% (Figure 4.5).

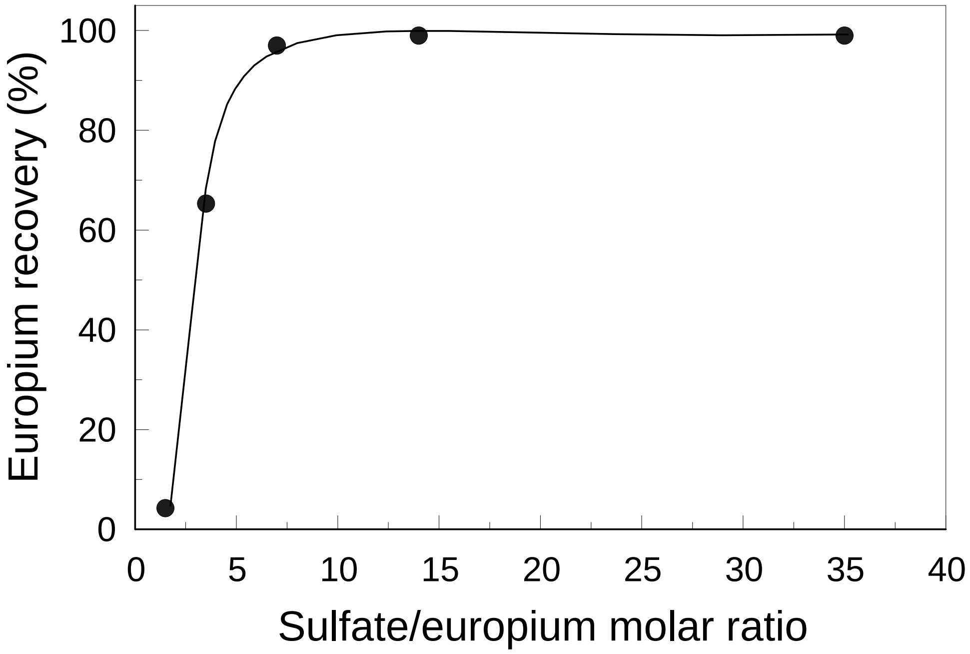

Figure 4. 5. Influence of the SO_4^{2-}/Eu molar ratio on europium recovery: 8×10^{-3} mol L^{-1} (1.25g L^{-1}) Eu_2O_3, molar ratio HCOOH/Eu = 600, 2 hours of irradiation.

The pH dependence on the Eu(III) photoreduction was investigated by Haas et al [22], who reported a maximum reduction between pH 1 to 1.5. Nevertheless, in that study, europium reduction was studied in terms of H_2 evolution and the authors did not make clear how the effects of pH on H_2 evolution and europium reduction were separated. In the present study, the pH varied from 0.8 to 0.3 as a result of varying sulfuric acid concentration. When ammonium sulfate was used as SO_4^{2-} source, the pH was maintained at 1.5. In this relatively large interval (pH 0.3 to 1.5), no effect of pH on europium recovery was detected.

When aiming at industrial applications, concentration becomes a key factor, affecting product recovery, grade and the overall process economics. Haas et al [22] studied the effect of concentration in the interval of 10^{-4} to 10^{-1} mol L^{-1} Eu^{3+}. The results indicated that europium reduction yields increased with concentration up to about 10^{-2} mol L^{-1} Eu^{3+} and then remained constant. Nevertheless, rather than being associated with concentration, the plateau may result from insufficient irradiation time and scavenger amount, which were maintained constant when europium concentration was increased. In other studies [13,19-21], europium concentrations were kept at 10^{-2} or 10^{-3} mol L^{-1}. In the present work, concentrations were varied from 6×10^{-3} to 5.7×10^{-2} mol L^{-1} Eu^{3+}. As expected, the irradiation time needed for a given europium recovery increases with concentration. Two hours of irradiation were sufficient to achieve approximately 99% europium recovery from a solution containing 1.25 g L^{-1} Eu_2O_3 ($7x10^{-3}$ mol L^{-1} Eu^{3+}). When concentration was doubled, four hours were required to achieve the same recovery (Fig.4.6). The relative amount of formic acid should also be considered. For a fixed 1.5 hours of irradiation, europium recovery attained 99% with a HCOOH/Eu molar ratio of 750, dropping to 74% with a HCOOH/Eu molar ratio of 600.

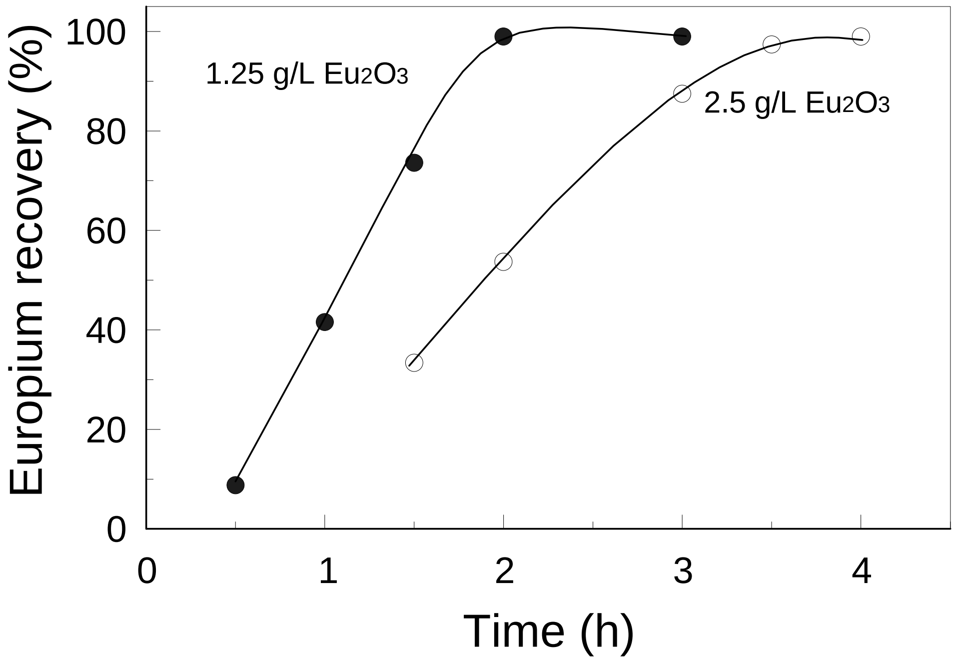

Figure 4. 6. Effect of feed concentration on europium recovery. 8×10^{-3} mol L^{-1} (1.25 g L^{-1}) Eu_2O_3, molar ratios: HCOOH/Eu = 600; SO_4^{2-}/Eu = 10.

When europium concentration was increased to 10.0 g L^{-1}, the precipitation of $Eu_2(SO_4)_3$ took place prior to irradiation. Considering the high solubility of trivalent rare earth sulfate salts in water, the phenomenon can be ascribed to the anti-solvent effect caused by the high concentration of scavenger required to maintain an adequate HCOOH/Eu ratio. High concentrations of organic compounds, such as formic acid and 2-propanol, decrease the dielectric constant of the medium, thus increasing the electrostatic attraction between the oppositely charged species (Eu^{3+}- SO_4^{2-}) and decreasing $Eu_2(SO_4)_3$ solubility. The effect also depends on sulfate concentration, which again, in order to maintain the ratio SO_4^{2-}/Eu, should increase with europium concentration. The previous results indicate difficulties in applying photochemical reduction to more concentrated solutions. This conclusion will be supported by the results shown in the following paragraphs.

The main goal of this work was to investigate the recovery of europium from an Eu/Gd solution. Most of the previous studies were carried out with equimolar, binary or ternary lanthanide mixtures, which do not properly represent the conditions found in many actual systems such as in ours. Now europium reduction from a solution with a Gd/Eu molar ratio of 27 is investigated. Tests were carried out varying sulfate, europium and HCOOH concentrations (Table IV.2). The irradiation time was fixed at 3 hours. Results with the pure europium solution with HCOOH/Eu molar ratio of 560 and SO_4^{2-}/Eu of 7 and europium concentration of 1.25 g L^{-1} Eu_2O_3 indicated that over 98% europium can be recovered as $EuSO_4$ in two hours of irradiation. Under similar conditions (HCOOH/Eu molar ratio of 600 and SO_4^{2-}/Eu molar ratio of 10) no precipitation took place with the Eu/Gd mixture. When SO_4^{2-}/Eu was varied from 10 to 120 and HCOOH/Eu was maintained at 600, solids were formed for SO_4^{2-}/Eu ratios above 60, but with no selectivity. In other series of experiments, the SO_4^{2-}/Eu molar ratio was fixed at 30 (4 times the one needed for maximum recovery with pure europium solutions) while the HCOOH/Eu ratio was varied from 800 to 1400. Precipitation took place for HCOOH/Eu ratios above 1200, but again with no selectivity. As an attempt to achieve selectivity, europium and gadolinium concentrations were reduced to half and ¼, respectively of the previous ones, whereas SO_4^{2-}/Eu and HCOOH/Eu molar ratios were chosen above the threshold for europium precipitation (Table IV.2). No precipitation was observed.

Measurements of the redox potentials indicated a final Eh_{298K} similar to that of the pure europium solution (-0.13V), thus suggesting that the difficulties were not related to this variable. Aimed at favoring nucleation, further experiments were carried out using $EuSO_4$ seeds. The other variables were maintained at HCOOH/Eu molar ratio of 600 and 1000, and SO_4^{2-}/Eu of 10 and 30. A comparison of the tests 1/13, 3/14 and 8/16 clearly indicates the role of the sulfate seeds in favoring precipitation, but again with no selectivity.

In conclusion, the experiments with a europium solution with high gadolinium concentrations led to two undesirable situations. In one, europium precipitation did not occur at all and in the other, europium and gadolinium were both precipitated.

Table IV.2: Experiments carried out with europium and gadolinium chloride solution

Test	Feed solution		Reagents and quantities		Recovery	
	Eu_2O_3 (g L^{-1})	Gd_2O_3 (g L^{-1})	SO_4^{2-}/Eu (mol/mol)	HCOOH/Eu (mol/mol)	Eu_2O_3 (%)	Gd_2O_3 (%)
1	1.0	27.6	10	600	0	0
2	1.0	27.6	20	600	0	0
3	1.0	27.6	30	600	0	0
4	1.0	27.6	60	600	8.7	6.3
5	1.0	27.6	100	600	15.3	11.7
6	1.0	27.6	120	600	75.5	68.5
7	1.0	27.6	30	800	0	0
8	1.0	27.6	30	1000	0	0
9	1.0	27.6	30	1200	7.0	7.2
10	1.0	27.6	30	1400	29.3	28.4
11	0.5	13.8	60	1400	0	0
12	0.25	6.9	120	2800	0	0
13*	1.0	27.6	10	600	21,6	14.1
14*	1.0	27.6	30	600	20.5	20.2
15*	1.0	27.6	10	1000	35.6	33.0
16*	1.0	27.6	30	1000	44.4	38.6

*0.01g of $EuSO_4$ added as seeds.

These results suggest that the use of photochemical reduction in aqueous phase is limited to dilute and relatively pure solutions, conditions not usually present in industrial application. The separation of Eu from a Sm/Eu/Gd mixture was investigated by Hirai et al [20,21] with solutions containing equimolar (0.005 mol L^{-1}) concentrations of $SmCl_3$, $EuCl_3$ and $GdCl_3$, which correspond to only 2.66 g L^{-1} total rare earth oxide (approximately 10% of that indicated in Table IV.2). For this very dilute system with formic acid, the coprecipitation of Sm-Gd limited the purity of europium precipitate to 90%. Donohue [19] also worked with equimolar mixture (0.01 mol L^{-1}) of binary or ternary lanthanide combinations. The separation factor, β, ([Eu/Ln](precipitated)/[Eu/Ln](initial)), was less than 5 for the light rare earths, and less than 300 for the heavy rare earths, thus showing the same lack of selectivity observed in the present work. A comparison of these separation factors may indicate that the anti-solvent effect caused by the presence of the scavenger is more accentuated for the light rare earths. Turning to the lack of precipitation, a possible lowering of free sulfate concentration, owing to its complexation with Gd is a possibility to be explored in order to explain the results obtained here. It is clear that a better understanding of the failure of photochemical reduction in Gd rich solutions should rely on a better comprehension of the solution chemistry of the system under consideration. Thermodynamic calculations together with activity coefficient determinations to estimate speciation and stability in the medium of interest may help to understand the cause of the failed separation.

The good results with dilute, relatively pure europium chloride solutions found in this and other works indicate the possibility of some niche applications for the photochemical reduction process in aqueous solution, such as the treatment of dilute rare earth solution or the removal of europium radionuclides from radioactive waste solutions. On the other hand, from the environmental point of view, one has to consider the large consumption (and further disposal) of organic compounds (scavengers) involved in the photochemical reduction of Eu(III) solutions. This aspect minimizes potential advantages with respect to the conventional process of europium reduction with zinc amalgam.

4.4. CONCLUSIONS

The factors influencing europium photoreduction/$EuSO_4$ precipitation were investigated by using a low-pressure mercury lamp (germicidal lamp) with photon emissions at 253.7 nm as light source. The main factors affecting europium recovery by photochemical reduction/precipitation were shown to be the total rare earth concentration, the sulfate/Eu molar ratio and the nature and the radical scavenger/Eu molar ratio. Europium recovery was shown to increase with the increase of SO_4^{2-}/Eu molar ratio up to 7. Similarly, high scavenger requirements (Formic acid/Eu ratio of 500) were needed to achieve high yields. A comparison between formic acid and 2-propanol used as scavengers indicated a faster kinetic reaction of the former (2 and 15 hours respectively). This was explained by photodecomposition of the formic acid, and the consequent increase in the reducing agent concentration and a fast decrease of Eh. The increase of europium concentration in the feed solution is limited by the anti-solvent effect caused by the presence of the scavenger, which in turn results in precipitation of this element as trivalent europium sulfate or the co-precipitation of gadolinium.

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CAPÍTULO 5

EUROPIUM (III) AND GADOLINIUM (III) SEPARATION BY SOLVENT EXTRACTION

ABSTRACT

This work was aimed at identifying suitable conditions for the separation of a europium/gadolinium mixture, with high Gd content, in one fraction of high purity gadolinium and the another of a enriched-europium Eu/Gd mixture, without previous europium reduction. Acid and basic extractants have been evaluated under several experimental conditions. Two acid extractants were investigated, the di (2-ethylhexyl phosphoric acid)-DEHPA and the 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)), the latter in its natural and saponified forms. Also, a series of basic extractant, Primene JM-T$^{®}$, Primene 81R$^{®}$ (primary amines), Alamina 336$^{®}$ (tertiary amine) and Aliquat 336$^{®}$ in chloride and nitrate form (tricaprylylmethylammonium choride and tricaprylylmethylammonium nitrate) were employed in the solvent extraction experiments. The extractant HEH(EHP) showed to more selective and more favorable for stripping compared to DEHPA. Among the basic extractants, the best results were obtained with Primene JM-T in sulfuric acid and with Aliquat-nitrate in nitric acid solutions. The selectivity achieved with these basic extractants (separation factor of 2.0) was superior to those obtained with the acid extractants (separation factors of 1.44 for DEHPA and 1.59 for HEH(EHP)).

Keywords: europium extraction, gadolinium extraction, europium/gadolinium separation

5.1. INTRODUCTION

The increasing interest for high-purity rare earth oxides, such as those of europium and gadolinium, can be explained by their diversified and expanding applications. Together with yttrium, europium is responsible for the red color in television screens and computer monitors. Gadolinium is employed in the medical field as contrasting agent in images obtained by magnetic resonance, as well as in the nuclear area, as absorber of thermal neutrons [1-6].

Europium, gadolinium and samarium are part of the middle rare earths group. The fractioning of this group into the individual elements is usually undertaken by the reduction of Eu(III) to Eu(II) and its precipitation as $EuSO_4$ [5-7], followed by Sm/Gd separation by solvent extraction [8,9]. An alternative route involves the removal of Sm, with susbsequent Eu/Gd separation by reduction of europium and precipitation of Eu(II) as $EuSO_4$.

In the present study, the separation of a Eu/Gd mixture with high gadolinium content (96.5 %wt. Gd_2O_3 and 3.5 %wt. of Eu_2O_3, in rare earths) was investigated without previous europium reduction. This mixture was obtained after the recovery of Sm by solvent extraction [10]. Studies of europium recovery by chemical reduction from this Eu/Gd mixture led to Eu_2O_3 99.99 %wt. in two reduction/precipitation stages [6]. Gadolinium (99.6±0.2 %wt) was then recovered from the filtrate of the europium recovery, by precipitation with oxalic acid or ammonium hydroxide. This product, however, is not adequate for the most noble applications, thus requiring further purification.

Although solvent extraction is not usually applied for Eu(III)/Gd(III) separation, the high gadolinium content (96.5 %wt. of Gd_2O_3) in the mixture has motivated the investigation of a partial Gd recovery prior to europium reduction. The advantages of this approach are (i) the reduction of the treated volume and the increase of europium concentration feeding the Eu recovery stage; (ii) the reduction of the number of reduction/precipitation stages required for the production of a high purity Eu_2O_3; (iii) the production of a higher yield, superior-value gadolinium oxide. In view of that, the objective of the present work was to identify the most favorable conditions for the separation of a Eu/Gd mixture into a phase of high purity Gd and a Eu-enriched mixture that would feed the subsequent europium recovery stage. Several basic and acids extractants were tested under various experimental conditions and the results obtained are discussed in detail.

5.2. EXPERIMENTAL

5.2.1. Reagents and Solutions

Europium and gadolinium solutions were prepared from a carbonate mixture of these elements (1.90%wt. Eu_2O_3 and 52.9%wt. Gd_2O_3) supplied by "INB-Indústrias Nucleares do Brasil". The chemical composition of this carbonate sample is presented on Table V.1. This characterization was accomplished by using X-ray spectrometry (lanthanides determination), atomic absorption spectrometry (ferric ion), potentiometry (chloride ion), and gravimetry (CO_3^{2-} and H_2O) methods. The aqueous solutions used in the experiments were prepared by dissolution of the Eu/Gd carbonates in hydrochloric and nitric acid solutions of concentration 3 mol L^{-1}. In the experiments with the basic extractants, the concentrations of chloride and nitrate were adjusted by the addition of the corresponding sodium salts. Eu/Gd sulfate solutions were prepared by reacting the carbonates with minimum amount of a concentrated solution (9 mol L^{-1}) of sulfuric acid, followed by the dissolution of the sulfates produced through the addition of distilled water. All solutions were prepared with analytical grade reagents and distilled water.

Table V.1: Chemical composition of Eu/Gd carbonates

Species	**Sm^{3+}**	**Eu^{3+}**	**Gd^{3+}**	**Tb^{3+}**	**CO_3^{2-}**	**Cl^-**	**Fe^{3+}**	**H_2O**
Content (wt.%)	<0.005	1.64	45.42	<0.005	43.30	2.30	0.06	7.28

Commercial extractants and organic solvents were used in this study. The extractants di 2-ethylhexyl phosphoric acid - DEHPA (97 %wt) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester - HEH(EHP) (96.5 %wt) were supplied by Albright & Wilson Americas, Inc. The primary amines (Primene JM-T®, Primene 81R®) were supplied by Rohm and Haas Company. Alamina 336® (tertiary amina), Aliquat 336® (tricaprylylmethylammonium choride), and tridecanol, used as a modifier agent, were supplied by “Cognis do Brasil Ltda”. EXXSOL® (purified kerosene), a diluent, was supplied by Exxon Chemicals Ltd.

The saponification of the HEH(EHP) was accomplished by contacting a solution 1.5 mol L^{-1} of this extractant with NH_4OH solution. Aliquat 336 (Aliquat-chloride) was converted to nitrate form (Aliquat-nitrate) by reacting a solution (0.5 mol L^{-1}) of this extractant with solutions of sodium nitrate (2 mol L^{-1}) in a volumetric (O/A) ratio of 2:1 for 5 minutes. This methodology, similar to that one used by Preston [11], has been modified in the present work by replacing the ammonium nitrate by sodium nitrate. The control of the conversion of the tricaprylylmethylammonium choride to tricaprylylmethylammonium nitrate has been controlled by the determination of the ion chloride concentration in the aqueous phase.

5.2.2. Experimental Procedure

The extraction experiments were carried out by mixing equal volumes (20 mL) of aqueous and organic phases in beakers of 100 mL, under mechanical agitation at 25°C. A contact time of 5 minutes was selected after preliminary experiments with the extractants, which indicated that equilibrium was attained in 3 minutes. After contact, the mixture was transferred to a separation funnel for phase separation. Experiments for determination of the separation factors were made in triplicates; the results indicated an error of 5%, for a confidence level of 95%.

The basic extractants were tested in chloride, nitric and sulfuric solutions. For nitric and chloride media, the concentrations of Eu_2O_3 and Gd_2O_3 were fixed at 1.0 and 27.6 g L^{-1}, respectively. The concentrations of chloride and nitrate were adjusted through the addition of the corresponding sodium salts. In sulfuric media, the concentrations of Eu_2O_3 and Gd_2O_3 were largely reduced (0.52 and 14.3 g L^{-1}) relatively to the previous ones due to the low solubility of these elements in sulfuric acid compared to these solubility in hydrochloric and nitric acids . The concentration of SO_4^{2-} was maintained constant at 1.0 mol L^{-1}. The initial pH value of the sulfuric acid solution was fixed at 1.0, while the pH in the chloride and nitric solutions were 1.0 and 3.0, respectively (no pH effects were observed in this range). The support experiments were made by Eu and Gd determinations in the aqueous phase. The measurements were made in an energy-dispersive X-ray spectrometer (Kevex sistem). This technique uses an Americium source (Am^{241}) for γ-rays generation and allows the detection of rare earths elements with a high sensibility level (10 μg g^{-1}) [12,13].

5.3. RESULTS AND DISCUSSION

The extractants commonly used in metal solvent extractions are classified as neutral, acids and basics. The neutral extractants act by a solvation mechanism, while acid and basic extractants operate by ion exchange. Acid extractants act through their conjugated bases and, therefore, they are classified as liquid cationic exchangers (Eq. 5.1 and 5.2). In Eq. (5.2), the extractant specie is presented as a dimer, which is the most common form for this class of reagent. The basic extractants are constituted by amines, which extract through their salts formed via protonation (Eq. 5.3). These salts extract anionic and neutral species by anionic exchange and formation of aductes, respectively (Eq. 5.4 and 5.5) [14,15].

$$nHA(org) + M^{n+} = MA_n\ (org) + nH \qquad (5.1)$$

$$n(HA)_2 + M^{n+} = M(A\text{-}HA)_n\ (org) + nH^+ \qquad (5.2)$$

$$nB(org) + nH^+(aq) + X^{n-}(aq) = (BH^+)_nX^{n-}(org) \qquad (5.3)$$

$$m(BH^+)_nX^{n-}(org) + nML^{m-}(aq) = n(BH^+)_m\ ML^{m-}(org) + mX^{n-}(aq) \qquad (5.4)$$

$$(BH^+)_nX^{n-}(org) + ML(aq) = (BH^+)_nX^{n-}ML(org) \qquad (5.5)$$

In the equations (5.1) to (5.5), A and B represent acid and basic extractants, respectively; M represents the metallic species; H^+ and X^{n-} constitute the acid specie in a dissociated form, and ML represents the metallic complex (L can be equal to X).

The separation of rare earths in the trivalent state is based upon the small and systematic difference in their basicity, that decrease from La to Lu in the lanthanide series [8]. This difference is due to the decrease of ionic radius with the increase in the atomic number of these elements, which is known as lanthanide contraction. In agreement with the basicity decrease, the acid extractants, which extracted by their conjugated bases, present higher affinity with the lanthanides of higher atomic number, which have more acidity character. The sequence in the case of the basic extractants will depend on the anion present in the aqueous phase. In nitric or sulfuric solutions, the behavior is the inverse of that observed for acid extractants, i.e., the extraction coefficient decreases with the increase of the atomic number. On the other hand, when the ligand is the thiocyanate ion (SCN^-), the extraction coefficient increases with the increase of the atomic number [11,16,17]. According to Preston and Du Prees [16], this behavior is due to the fact that the metal interaction with thiocyanate, a monodentate ligand, is dominated by electrostatic interactions, thus being favored by the increase of the cation atomic number. The results indicate the absence of steric constraints. In the case of nitrate, the steric effects predominate, presumably due to the high coordination number required for the binding of three or more bidentate nitrate ligands. For sulfate medium, which is also a bidentate ligand, similar trend to that of nitrate is observed.

5.3.1. Basic Extractants

Based on the chemical composition of the mixture investigated in this study, basic extractants appear as most suitable for the separation purposes. This hypothesis relies on the fact that europium is a minor constituent and has smaller atomic number than gadolinium. Thus, europium could be preferentially extracted to gadolinium. However, the efficiency of amines depends on the medium and, in particular, on its capacity to form neutral or anionic complexes with the metals to be extracted. The results discussed below illustrate these observations. Table V.2 shows the results obtained with primary, terciary amines and a quaternary ammonium salt. High nitrate concentrations were required because it is quite difficult do form neutral or anionic complexes with europium and gadolinium. On the other hand, significantly lower concentration levels with SO_4^{2-} could be used because anionic rare earth complexes are easily obtained at sulfuric medium.

Table V.2:Extraction of europium and gadolinium with basic extractants.

Experiment	**Organic phase**	**Aqueous phase**		**Extraction (%)**		**S.F.**
Number	Extractant	Solution	Conc. (mol/L)	Eu_2O_3	Gd_2O_3	Eu/Gd
1	Primene 81R	SO_4^{2-}	1.0	88.4	79.0	2.0
2	Primene JM-T	SO_4^{2-}	1.0	99.1	98.4	1.8
3	Primene JM-T*	SO_4^{2-}	1.0	66.1	48.9	2.0
4	Alamina 336	NO_3^-	4.0	10.3	8.9	1.2
5	Aliquat-nitrate	NO_3^-	4.0	15.5	8.3	2.0
6	Aliquat-nitrate	NO_3^-	6.0	25.8	14.7	2.0
7	Aliquat-nitrate	NO_3^-	8.0	43.3	27.5	2.0

Extractants concentration = 0.5 mol L^{-1}, *Extractant concentration = 0.25 mol/L, S.F. = separation factor, Conc. = concentration.

The experimental results obtained in sulfuric acid solutions indicated higher metal extraction levels with Primene JM-T in comparison with Primene 81R (experiments 1 and 2). In these experiments, the separation factor obtained with Primene JM-T is lower because of the extraction percentage with Primene JM-T was nearly 100% for both metals. The same separation factor was achieved when the concentration of Primene JM-T was halved (experiment 3). The contact of these extractants with hydrochloric and nitric acid solutions resulted in formation of stable emulsions, so these chemicals were excluded from the study.

In contrast to the observed behaviour of the primary amines, both Aliquat (in chloride and nitrate forms) and Alamina 336 in sulfuric medium resulted in inefficient metal extraction. This is probably due to steric effects associated with the large size of the molecules of $[Eu(SO_4)_2]^-$ and $[Gd(SO_4)_2]^-$ complexes. This effect was not observed using primary amines because, in this case, the amino group is either free or linked to nitrogen by only one carbon chain. Alamina and Aliquat present three carbonic chains linked to the nitrogen atom. Also, no extraction with Alamina 336 and Aliquat-chloride has been observed in hydrochloric medium. This is due to the predominance of the cationic complexes, $[EuCl]^{2+}$, $[EuCl_2]^+$, $[GdCl]^{2+}$ and $[GdCl_2]^+$ or free metallic cations, Eu^{3+} and Gd^{3+}, which are not extracted by amines. In these experiments, Cl^- concentrations were tested until the saturation level of NaCl, i.e., 4.0 mol L^{-1}, was reached. In nitric solutions, Aliquat-nitrate showed better selectivity than Alamina 336, as indicated by the separation factors in the experiments 4 and 5 respectively (table V.2). The effect of the nitrate concentration on the extraction of Eu and Gd is observed by the increase of this anion concentration from 4 to 8 mol L^{-1} (experiments 5, 6 and 7). The increase in metal extraction is attributed to the fact of higher nitrate concentrations favor the formation of neutral complexes of the type $[Eu(NO_3)_3]$ and $[Gd(NO_3)_3]$, which are extracted by amines [16].

Summarizing, the best results (separation factor of 2.0) were obtained with the primary amines (Primene 81R and Primene JM-T) in sulfuric solutions and with Aliquat-nitrate in nitric solutions. The difference between the two primary amines is the number of carbon atoms in the alquil group: Primene 81R with 12 to 14 carbons and Primene JM-T with 16 to 22 carbons (more hydrophobic character). Due to the high dispersion of the organic in the aqueous phase, Primene 81R, was excluded, and the subsequent studies were carried out with Primene JM-T and Aliquat-nitrate.

The effect of extractant concentration, the saturation metal in the organic phase and the metal stripping condition are investigated below with the two selected extractants: Primene JM-T and Aliquat-nitrate. Has been found that the variation in the concentration of Primene JM-T from 0.1 to 0.3 mol L^{-1} did not affect the separation factor for Eu/Gd. The saturation of Primene JM-T (0.5 mol L^{-1}) was already observed in the first contact, at 14.8 g L^{-1} of total oxides (Eu_2O_3 + Gd_2O_3). In the case of Aliquat-nitrate, the saturation level was 10.6 g L^{-1} for the above mentioned oxides, after 4 successive contacts with the same organic solution. The stripping of europium and gadolinium from the loaded Aliquat-nitrate solution showed to be non metal selective, so both Eu and Gd were completely stripped with water. In the stripping experiments with the loaded Primene JM-T, the concentration of sulfuric acid varied from 0.25 to 2.0 mol L^{-1} and a separation factor Eu/Gd of 1.7 was attained. Based on these results, the following difficulties in the separation of europium and gadolinium with basic extractants can be pointed out: (i) the saturation of Primene JM-T occurs even in the first contact, (ii) there is no selectivity in the metal stripping from the loaded Aliquat-nitrate and (iii) high nitrate concentrations are required in the extraction with Aliquat-nitrate.

5.3.2. Acid Extractants

The study has focued also the extractants DEHPA and HEH(EHP) (natural and saponified forms) in hydrochloric acid media. It is well known that the hydrogen ions released in the ion-exchange process (Eq. 5.2 and 5.3) affect negatively the metal extraction due to the increase of acidity in the aqueous phase. This problem can be partially solved by saponification of the extractants, thus leading to a predominant release of sodium, potassium or ammonium ions. Partial saponification is recommended to avoid the problems of formation of a gel phase and loss of extractant due to solubilization [18,19]. The experiments with acid extractants investigated the influence of the concentration of rare earths in the aqueous phase, the acidity of the Eu/Gd solution and the concentration of the extractants. The goal was the removal of the major constituent (Gd), so the experiments were carried out in a relatively high extractant concentration (1.5 mol L^{-1}). The results are shown in Table V.3.

Table V.3: Extraction of Europium and Gadolinium with DEHPA, natural HEH(EHP) and saponified HEH(EHP).

Extractant	**Extraction (%)**		**Extraction Coefficient**		**S.F.**
	Eu_2O_3	**Gd_2O_3**	**Eu**	**Gd**	**Gd/Eu**
DEHPA	38.2	47.0	0.613	0.910	1.44
Natural HEH(EHP)	18.8	26.9	0.232	0.368	1.59
Saponified HEH(EHP)	23.7	32.9	0.309	0.489	1.58

Feed solution: 2.50 g L^{-1} Eu_2O_3 and 69.1 gL^{-1} Gd_2O_3, pH 3.0.

In opposite to the results obtained with amines, the extraction of Gd with acid extractants is superior to the extraction of Eu (Table V.3). Higher extractions were achieved with DEHPA as compared to natural HEH(EHP). In the case of the saponified HEH(EHP), the extraction was 20% superior to that obtained with natural HEH(EHP) but still inferior to that obtained with DEHPA. Although DEHPA has presented larger extraction coefficients compared to EHE(EHP), the separation factor obtained with DEHPA was slightly inferior to the observed with HEH(EHP). Saponification has shown not to improve the Gd/Eu separation factors. The increment observed in metal extraction is not substancial enough to justify saponification of HEH(EHP). Also, the loss of 0.05 mol L^{-1}, which is small in a laboratory scale experiment, can become significant after several stages of solvent recycling. Thus, subsequent extraction studies were accomplished with natural HEH(EHP) and DEHPA. In these experiments, the concentration of these extractants (Fig. 5.1), the pH of the aqueous chloride solution (Fig. 5.2) and the concentration of Eu/Gd in the feed solution (Fig. 5.3) were investigated. The influence of hydrochloric acid concentration in metal stripping was also investigated (Fig. 5.4).

The extractants concentration used in this study ranged from 0.5 to 1.5 mol L^{-1}. As expected, metal extraction increases with the increase of extractant concentration. Nevertheless, the parallel curves shown in Fig V.1 indicate that no gain in selectivity was obtained with both extractants for the concentration range studied. The extractants concentration used in the subsequent studies was fixed at 1.5 mol L^{-1}.

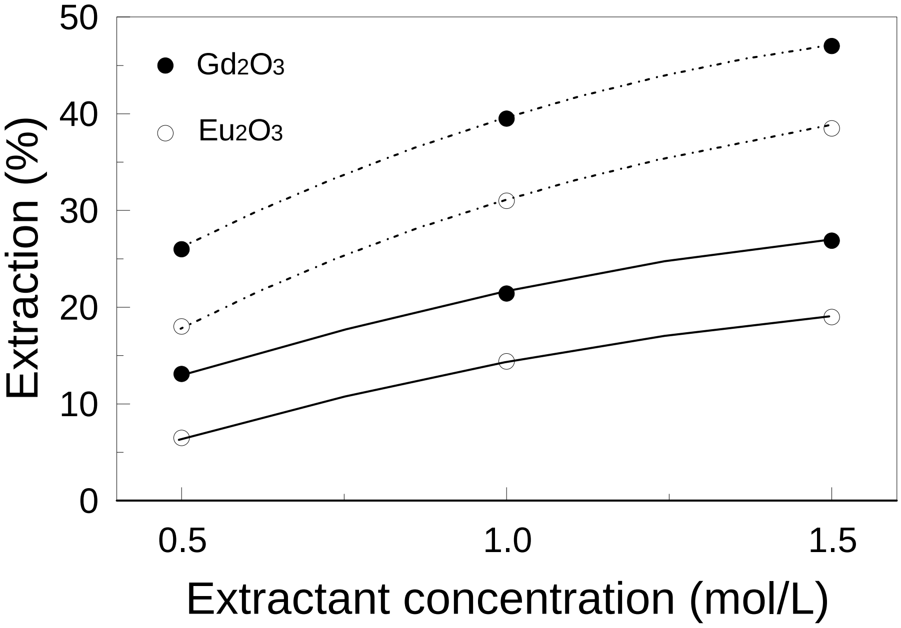

Figure 5.1. Influence of DEHPA and EHE(EHP) concentration on Eu and Gd extraction. The dotted lines indicates the experiments accomplished with DEHPA. Feed solution: 2.50 g L^{-1} Eu_2O_3 and 69.1 g L^{-1} Gd_2O_3, pH 3.0.

The acidity of the feed solution is usually a variable of great importance in the solvent extraction process and, in many cases, is a determinant factor in the process selectivity. The influence of acidity in metal extraction was investigated from pH 0 to 3. As shown in Fig. 5.2, the extraction increases up to pH one with both extractants and then reaches a plateau. The effect is more pronounced with HEH(EHP). No improvement in selectivity was observed in the pH range studied.

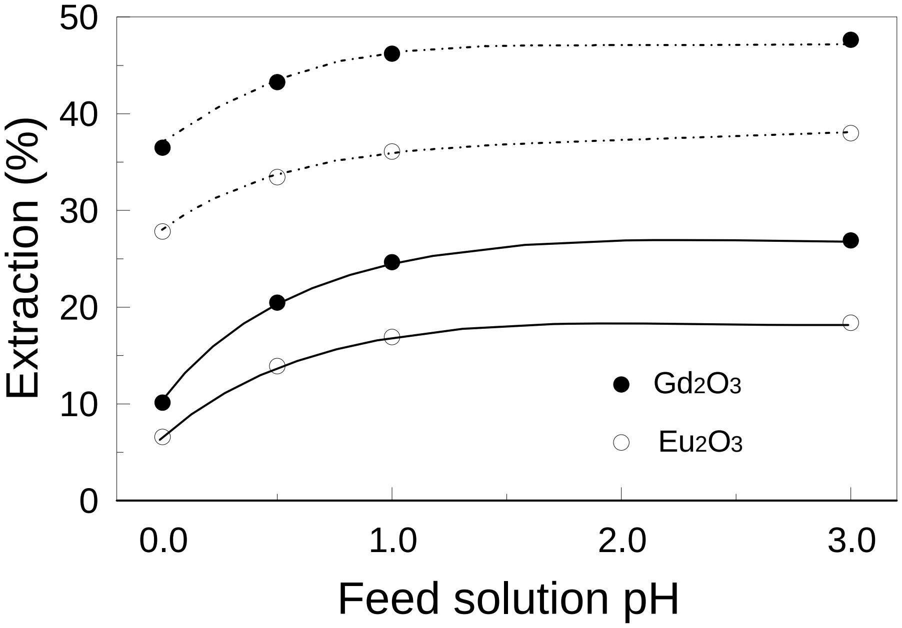

Figure 5.2. Effect of the chloride solution acidity on Eu and Gd extraction with DEHPA and EHE(EHP). The dotted lines indicates the experiments accomplished with DEHPA. Feed solution: 2.50 g L^{-1} Eu_2O_3 and 69.1 g L^{-1} Gd_2O_3.

In order to investigate the effect of Eu/Gd concentration on metal extraction, the feed solution used in the previous experiments was diluted 1.5, 2.0 and 2.5 times. The obtained results are presented in Fig. 5.3. As expected, the extraction increases as metal concentration decreases for the same extractant concentration. In the experiments accomplished with DEHPA, europium and gadolinium curves almost touch each other in the point of smallest concentrations. This indicates that, in continuous experiments, as the Gd concentration decreases, europium extraction will reach the same levels of gadolinium extraction. This undesirable behavior was not observed with HEH(EHP) but, in this case, the extraction levels were significantly lower to that obtained with DEHPA.

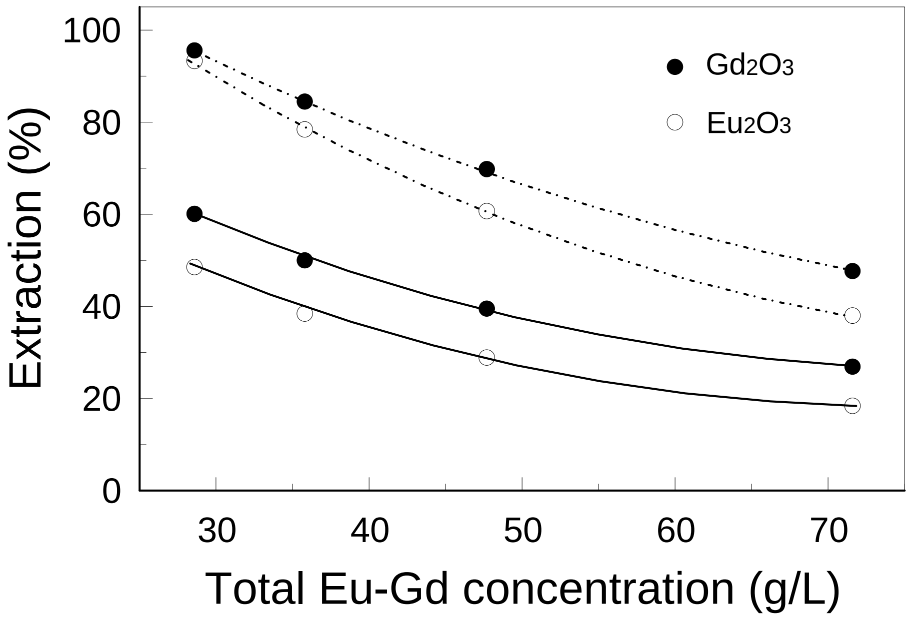

Figure 5.3. Effect of the total Eu and Gd concentration in the chloride solution (pH=3.0) on the individual elements extraction with DEHPA and HEH(EHP). The dotted lines indicates the experiments accomplished with DEHPA.

Finally, the influence of HCl concentration on the metal stripping from the loaded extractants was investigated. In these studies, the HCl concentration was varied from 0.25 to 2.0 mol L^{-1}. As it can be observed, the stripping of both metals is much easier accomplished with HEH(EHP) than with DEHPA. Europium is quite totally stripped out using EHE(EHP) in hydrochloric medium (1.0 mol L^{-1}), while for DEHPA, the double of this acidity extracted only 86.3% of Eu and 74.2% of Gd (Fig. 5.4). According to this result, a more diluted acid solution can be employed in the scrubbing and stripping stages when HEH(EHP) is used. Based in the separation factors obtained with HEH(EHP) and their easier stripping, HEH(EHP) seems to be the best option, compared to DEHPA, for further studies in a continuous circuit.

Among the basic extractants, modified Aliquat 336 presented the advantage of non-saturation in only one contact. The lack in selectivity during metal stripping may be overcome by the use of higher organic/aqueous ratios.

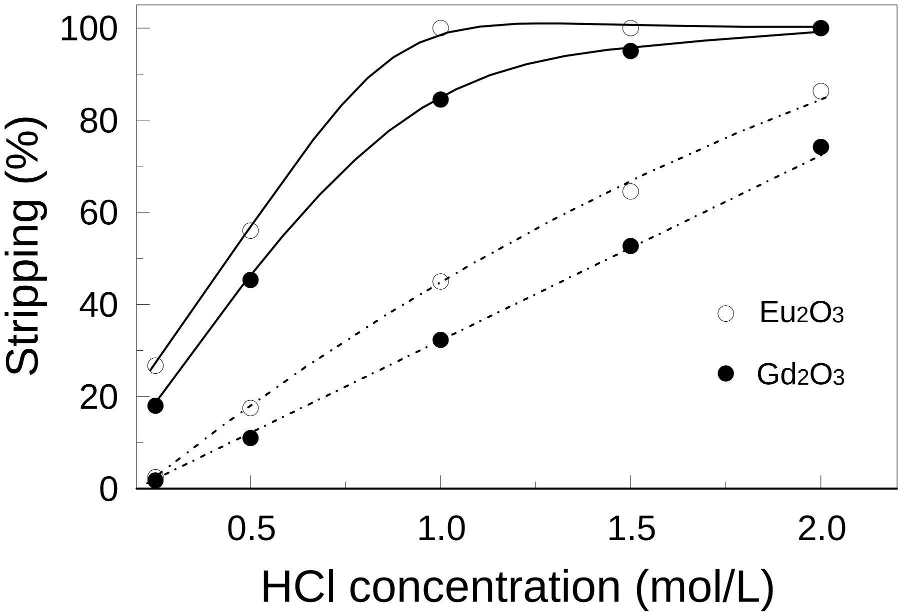

Figure 5.4. Effect of the HCl concentration on the Eu/Gd stripping from loaded DEHPA and EHE(EHP). The dotted lines indicates the experiments accomplished with DEHPA. Organic phases: 0.8 g L^{-1} Eu_2O_3 and 31.5 g L^{-1} Gd_2O_3

5.4. CONCLUSIONS

Our studies confirme the difficulties in the separation of Eu/Gd when both elements are in the trivalent state. The reagent HEH(EHP) presented higher separation factor and it seems to be more suitable for metal stripping compared to DEHPA. Although the difference in the separation factors is small, it may become more significant under continuous operation. Saponification of HEH(EHP) showed no detectable advantage considering that the separation factors remained unaffected. For the basic extractants, the best results were obtained with Primene JM-T in sulfuric medium and with Aliquat-nitrate in nitric solutions. The selectivity achieved with the basic extractants (separation factor of 2.0) was superior to those obtained with the acid extractants (1.44 for DEHPA and 1.59 for HEH(EHP).

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CAPITULO 6

PROCESS DEVELOPMENT FOR THE RECOVERY OF HIGH GRADE LANTHANUM BY SOLVENT EXTRACTION

ABSTRACT

The development of a solvent extraction process for the recovery of high-grade lanthanum oxide from a light rare earth (La, Pr, Nd) chloride solution is described. In a preliminary stage, process parameters and experimental conditions were explored in bench-scale experiments. The effect of variables such as nature and concentration of the extractant (DEHPA and HEH(EHP)), contact time, acidity and rare earth concentration in the extraction stage as well as the effect of the hydrochloric acid concentration in the stripping stage were investigated. The continuous counter-current experiments were carried out in a mini-battery unit of mixers-settler. The final set-up was comprised by twenty-two stages: 8 for extraction, 8 for scrubbing and 6 for stripping. A high-grade oxide (>99.9% La_2O_3) was obtained with a yield superior to 99.9%.

Keywords: lanthanum, lanthanum recovery, lanthanum extraction

6.1. INTRODUCTION

Rare earths (RE) elements have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high-temperature superconductors and secondary batteries, catalysis, red phosphors, among others [1-5]. Lanthanum, one of the most abundant of the lanthanides, is an important element of mischmetal and hydrogen-absorbing alloy [5]. The RE elements occur together in nature in some minerals like bastnasite, monazite, xenotime, and others [1,4]. The high value of these elements depends on its effective separation into high purity compounds. The separation of the natural RE mixtures into the individual elements is very difficult to achieve, due to the very low separation factors involving the adjacent RE elements [6]. Among the trivalent lanthanides, Ce and Eu can be separated through changes in their oxidation state. The Ce(III) is oxidized to Ce (IV) and the Eu (III) is reduced to Eu (II) [7-9]. The separation of the other RE elements, usually carried out by solvent extraction or ion exchange, is based on systematic differences in their basicity, which decreases from La to Lu [4,7]. Generally, a mixture of rare earths is first separated into groups of: light rare earths (La, Ce, Pr, Nd), middle rare earths (Sm, Eu, Gd) and heavy rare earths (Tb, Dy Ho, Er, Tm, Yb, Lu, Sc, Y). This separation is favored by the relatively higher separation factor between Nd/Sm and Gd/Tb compared to the others within a group. It is usually accomplished by solvent extraction, using di-2-ethylhexilphosphoric acid (DEHPA) as the extractant [2,4].

The extraction behavior of rare earths has been studied since the 50’s. There are several reports on the separation of rare earth elements in different media and extractants, such as: phosphoric, phosphonic and phosfinic acids, with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) also known as 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA) and DEHPA being the most used [3,5,6, 10-24]; neutral phosphate, such as Tri-n-butylphosphate (TBP) and tri-n-octylphosphine oxide (TOPO) [25-27]; carboxylic acid derivative [23,28]; amines [29-31]; ketones and others [31,32]. The great majority of these studies focus on the fundamentals, which include the determination of separation and extraction parameters in synthetic solutions, evaluation of kinetics and reaction mechanism, among others. There is little information in the literature regarding process development, mainly for proprietary reasons.

DEHPA is one of the first and most extensively investigated extractant in the separation of the rare earth elements. In recent years, studies have been also carried out with HEH(EHP) in view of some advantages compared to DEHPA, like higher separation factors and easier stripping [10,11]. In this work, the use of DEHPA and HEH(EHP) for the separation of lanthanum from a light rare earth chloride liquor was investigated. A process to obtain a high-grade La_2O_3 using HEH(EHP) as extractant was developed and is now described.

6.2. EXPERIMENTAL

6.2.1. Reagents and Solutions

The extractants, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester - HEH(EHP) (96.5 %wt), commercialized with the trade name Ionquest 801® and di-2-ethylhexilphosphoric acid - DEHPA (97 %wt), were supplied by Albright & Wilson Americas Inc. The extractants were diluted in Exxsol® (purified kerosene), supplied by “Exxon Química Ltda.”. All other reagents were of analytical grade and their solutions prepared with distilled water**.**

The rare earth chloride solution was supplied by “INB – Industrias Nucleares do Brasil S.A.”. Prior to the experiments, cerium was recovered through oxidation/hydrolysis with $KMnO_4$/Na_2CO_3 solution [33]. The filtrate containing the remaining light rare earths was neutralized with Na_2CO_3 solution in order to separate the RE from the permanganate excess, and to obtain the RE carbonate. The chemical composition of the chloride liquor and the RE carbonate are shown in Table VI.1. The light RE solution used in the experiments was prepared by dissolving the RE carbonate in an aqueous hydrochloric solution (3.0 mol L^{-1}).

Table VI.1: Chemical composition of the light RE liquor and the RE carbonate, after cerium removal

Sample	**La^{3+}**	**Ce^{3+}**	**Pr^{3+}**	**Nd^{3+}**	**Sm^{3+}**	**CO_3^{2-}**	**Cl^-**	**H_2O**
Hydrochloric liquor (g L^{-1})	138	17.3	29.2	110	0.42	-	550	-
RE carbonate (% wt.)	32.8	0.07	6.89	26.2	0.10	33.1	0.35	5.8

6.2.2. Batch Experiments

The main process parameters, such as aqueous phase acidity, RE concentration, nature and concentration of the extractant on the extraction stage and the effect of the hydrochloric acid concentration on the RE stripping from the loaded organic phase were investigated. The experiments were carried out in mechanically agitated beakers containing equal volumes (20 cm^3) of the aqueous and organic phases, at (25 ± 1) ^oC. Following contact, the phases were separated in a funnel. All the batch experiments were carried out at a fixed contact time of 5 min., based on the results of preliminary experiments indicating that 3 minutes were sufficient to achieve equilibrium.

6.2.3. Continuous Experiments

The continuous experiments were carried out using HEH(EHP) as extractant, in an acrylic mini-battery unit of mixers-settlers, supplied by Sonal-Polux, with mixers of 13 cm^3 and settlers of 40 cm^3 capacities, each run lasting 30 hours. The solutions were fed by peristaltic pump into six points of the circuit. These solutions were the RE and organic solutions, ammonium hydroxide solution for pH adjustment in the extraction stage, the scrubbing and the stripping solutions. The control of the process stability was made by lanthanides determination in the exit flows in every hour. At this time the flow rate of the feeding solutions were also checked. In the development of the process, the lanthanide concentrations were mostly measured in the aqueous phase by using an energy-dispersive X-ray spectrometry (Kevex system). The minor constituents were determined by an atomic emission spectrometer with inductively coupled plasma (ICP/AES).

The Kevex system has a radioactive source of americium (Am^{241}) with 100 mCi of activity for the X-ray generation. The complete setup is built around an Si(Li) detector X-ray spectrometer, with an energy resolution of 220 eV at 5.94 KeV. The peaks observed in the X-ray fluorescence spectra are fitted with a multicomponet spectrum analysis and the intensities of the characteristic X-ray lines are extracted, for calculating the elemental concentrations. Specifically for the rare earth elements, Am^{241}, is the indicated radioisotope as source to produce the fluorescence. The X-ray spectrum formed is due to the K layer excitement, which produces simpler spectra compared to those obtained by the L layer. Another advantage of the Kevex system is the fact of the analysis can be undertaken in solid and liquid samples. The detection limit of this technique depends on the atomic number of the element and the counting time. For the rare earth elements, this limit is of few micrograms per gram [9].

6.3. RESULTS AND DISCUSSION

DEHPA and HEH(EHP) are liquid cation-exchangers, the extracted metal being exchanged by the hydrogen ion in the hydroxyl group. Figure 6.1 shows the structural formulae for both reagents.

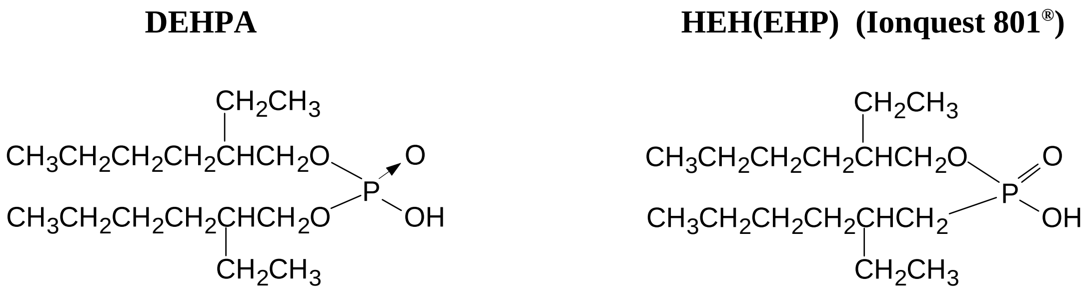


Figure 6.1. Structural formulae of the extractants DEHPA and HEH(EHP)

These reagents are prone to form dimer through hydrogen bonding. In dilute solutions, the dimerization increases with the decrease of solvent (diluent) polarity [12-14]. Concentrate solutions, like those required in industrial processes, favors the formation of dimeric forms, generally represented by $(HX)_2$ or H_2X_2.

The mechanism involved in the extraction of rare earths by DEHPA and HEH(EHP) was first described by Peppared and collaborators [15,16]. The mechanism, later confirmed by others [19-22], can be represented by the following reaction:

$$RE^{3+}_{(aq)} + 3(HX)_{2(org)} \; = \; REX_3.3HX_{(org)} + 3H^{+}_{(aq)} \qquad (6.1)$$

Where HX symbolizes the extractant molecule and X its deprotonated form.

Mechanisms of rare earth extraction by DEHPA involving the formation organic species like $REX_3.2HX$ and REX_3 were also indicated [3,14,17,21,22]. These species are believed to occur in very dilute organic solutions, where dimerization of DEHPA is not significant and the extractant also exists as a monomer [14]. At high organic concentrations such as those applied in this investigation, the monomer form can be neglected, with the predominance of the mechanism shown in Eq. (6.1).

6.3.1. Batch Experiments

The batch experiments were carried out with the extractants DEHPA and HEH(EHP). The following variables were investigated: extractant concentration, acidity and concentration of rare earths in the feed solution, contact time in the metal extraction and stripping and hydrochloric acid concentration in the metal stripping. The results are presented in Figures 6.2 to 6.5.

Figure 6.2 shows the extraction of La, Pr and Nd as a function of extractant concentration. More concentrated feed solutions, such as those used here, required higher extractant concentration. It can be observed that the extraction increases as the extractant concentration increases from 0.5 to 2 mol/L, the increase being relatively higher in the case of DEHPA. Also, for all three elements, significantly higher extraction is obtained with DEHPA. The selectivity of both extractants with respect to Pr and Nd is clearly indicated. Extractions of Pr and Nd, are quite similar for both extractants. The increase in the extraction from La to Nd can be explained by the difference in the acidity of these elements, which increases from La to Lu. This difference is related to a systematic and smooth decrease in the ionic radii of the RE elements, known as the lanthanide contraction, which increases with the atomic number in the lanthanide series [1,4]. The very low extraction of La with HEH(EHP), should be emphasized as this will help separation of this rare earth from the mixture. The subsequent experiments were carried out with the extractans concentration of 1.5 mol L^{-1}.

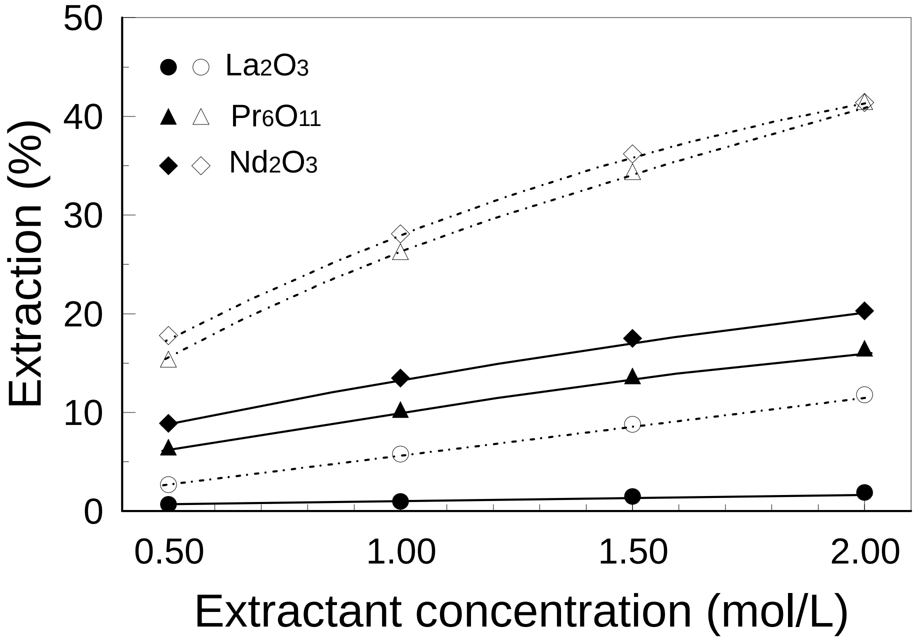


Figure 6.2. Influence of DEHPA and EHE(EHP) concentration on the RE elements extraction. The dotted lines represents the experiments with DEHPA. Feed solution: 44.0 g L^{-1} La_2O_3, 9.33 g L^{-1} Pr_6O_{11}, 35.7 g L^{-1} Nd_2O_3, pH 2.4.

The pH of the aqueous phase was investigated from 0 to 2.4. As shown by (Eq. 6.1), the extraction increases with the decrease of the acidity of the RE earth solution. With both extractants, the extraction increases up to pH one and then reaches a plateau (Fig. 6.3). For all three metals, the extraction with HEH(EHP) drops to nearly zero as pH reaches values less than 0.5. This indicates that the use of this reagent would require a very effective pH control in the extraction stage.

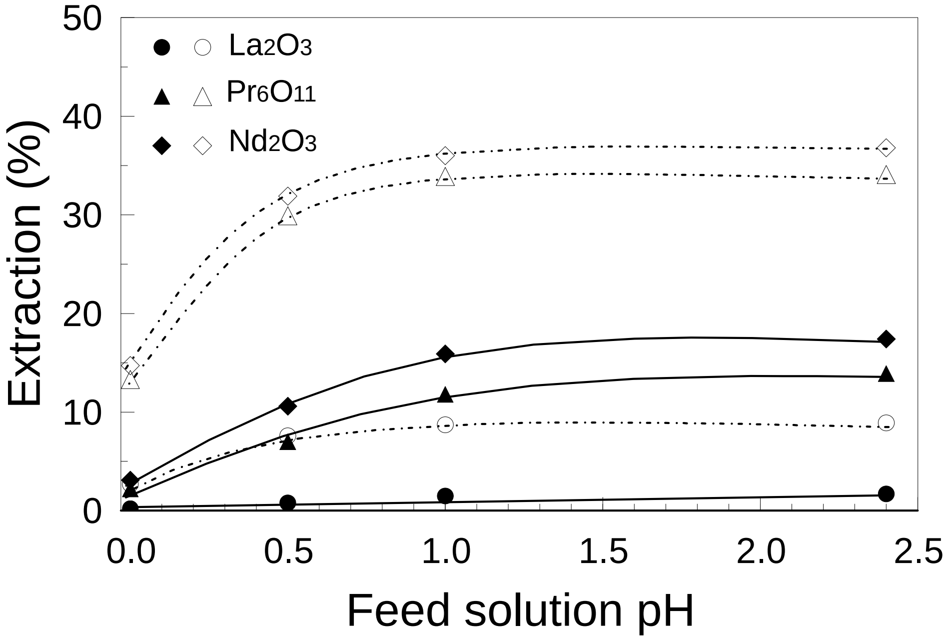


Figure 6.3. Effect of the chloride solution acidity on the RE elements extraction with DEHPA and HEH(EHP). The dotted lines represents the experiments with DEHPA. Feed solution: 44.0 g L^{-1} La_2O_3, 9.33 g L^{-1} Pr_6O_{11}, 35.7 g L^{-1} Nd_2O_3.

The total rare earth concentration was investigated from 30 to 89 g L^{-1} RE oxides. As expected, extraction increases as the total rare earth concentration decreases (Fig. 6.4). Among all the studied variables, this was the one that caused the most significant influence on selectivity. This happens because the decrease in the RE concentration caused a relative higher increase in lanthanum extraction as compared to the increase in the extraction of praseodymium and neodymium. Though it is not obvious by the distances between the lines shown in Fig. 6.4, these differences will reflect in a significant reduction in the separation factor Pr/La, as the RE concentration decreases (Table VI.2). The separation factor indicates the easiness in the separation of two elements; it is calculated by the ratio of the extraction coefficients of these elements obtained under the same experimental conditions. For the system HEH(EHP)-HCl, the separation factor Pr/La increased from 7.7 to 10.2 while for the system DEHPA-HCl, it varied from 4.6 to 5.4, as total RE concentration varied from 29.7 to 89.0 g L^{-1}.

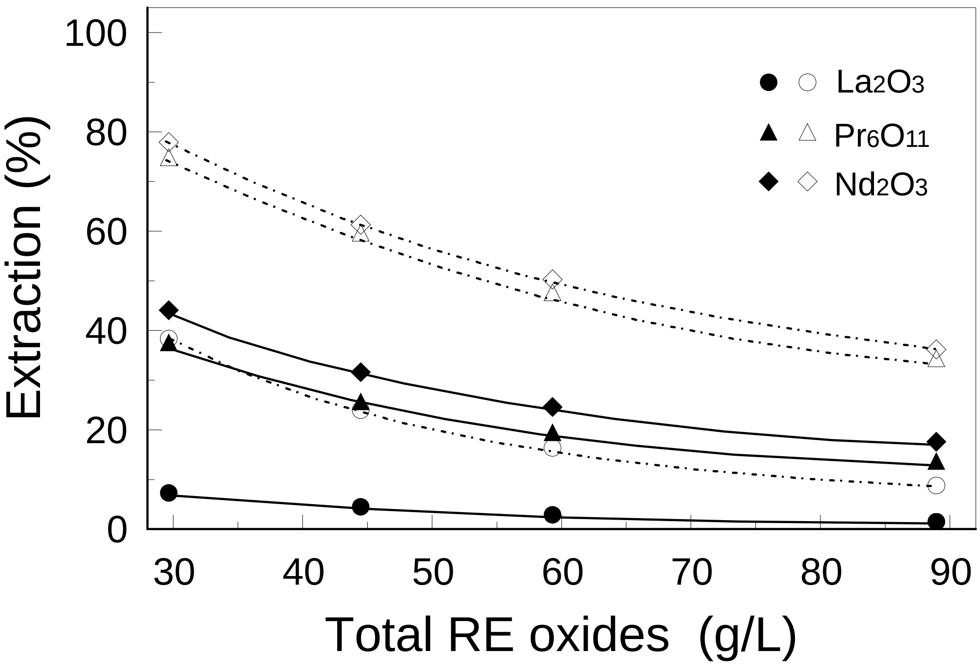


Figure 6.4. Effect of the total RE concentration on the individual elements extraction with DEHPA and HEH(EHP). The dotted lines represents the experiments with DEHPA. Feed solution pH 2.4.

Table VI.2: Extraction coefficient of La, Pr and Nd and separation factor of Pr/La and Nd/Pr for different La, Pr and Nd concentration.

Extratant	Total RE oxide (g L^{-1})	Extraction coefficient			Separation factor	
		LaE^o_a	PrE^o_a	NdE^o_a	Pr/La	Nd/Pr
HEH(EHP)	89.0	0.016	0.163	0.217	10.2	1.33
HEH(EHP)	59.3	0.026	0.242	0.324	9.31	1.34
HEH(EHP)	44.5	0.045	0.346	0.460	7.69	1.33
HEH(EHP)	29.7	0.082	0.605	0.798	7.38	1.32
DEHPA	89.0	0.096	0.520	0.570	5.42	1.10
DEHPA	59.3	0.191	0.914	1.015	4.79	1.11
DEHPA	44.5	0.316	1.484	1.622	4.70	1.09
DEHPA	29.7	0.652	2.987	3.250	4.58	1.09

Feed solution: 49.4 % wt. La_2O_3, 10.5 % wt. Pr_6O_{11}, 40.1 % wt. Nd_2O_3, pH 2.4; extractants concentration: 1.5 mol L^{-1}.

The separation factors Nd/Pr remained practically constant and equal to 1.3, for the system HEH(EHP)-HCl, and 1.1 for the system DEHPA-HCl. As for Pr/La, the highest separation factors were obtained with HEH(EHP)-HCl. The separation factor was not significantly affected by the other variables investigated in the present study, maintaining at 10.2 and 1.33 for La/Pr and Pr/Nd, respectively with HEH(EHP) and 5.4 and 1.10 with DEHPA. The high separation factor between La and Pr is due the absence of cerium and the higher basic character of lanthanum.

Under all conditions, the extractions obtained with DEHPA were significantly superior to those obtained with HEH(EHP). These results will be discussed on the basis of the soft and hard acid/base theory [34,35] and the hydrophilic character of the different extractants. DEHPA and HEH(EHP) are cationic extractants, thus the analysis of their extraction behavior should take into consideration their conjugated bases. DEHPA is a stronger acid than HEH(EHP) (pKa 3.2 and 4.4 at 298 k, respectively) having, hence, by the Lewis acid/base theory, a weaker conjugated base than HEH(EHP). For this reason, lower extractions would be expected for DEHPA, which is not the case. The pKa of the reagents was determined experimentally in this work by titration, the pKa being the pH in the half of equivalent volume [36]. The soft and hard acid/base theory divides acids and bases into 2 categories: polarizable or “soft” and nonpolarizable or “hard”. As hard acids, the lanthanide ions will prefer to bind to hard bases[34]. It is hypothesized here that the symmetry of the 4 oxygen atoms around the phosphorus atom in DEHPA would be responsible for making the conjugated base of this extractant harder than the conjugated base of HEH(EHP). In addition to and perhaps even more relevant is the relatively higher hydrophilic nature of the phosphate group in DEHPA as compared to the phosphonic group in HEH(EHP), thus making the former more active in the organic/aqueous interface.

As the extraction of the rare earths is higher with DEHPA compared to HEH(EHP), metal stripping, the reverse reaction, is expected to be relatively easier from the loaded HEH(EHP) as compared to DEHPA. This behaviour is confirmed by the results shown in Figure 6.5. Lanthanum is fully stripped from HEH(EHP) with 0.25 mol L^{-1} HCl solution while 1.5 mol L^{-1} HCl was required for the complete stripping of lanthanum from DEHPA.

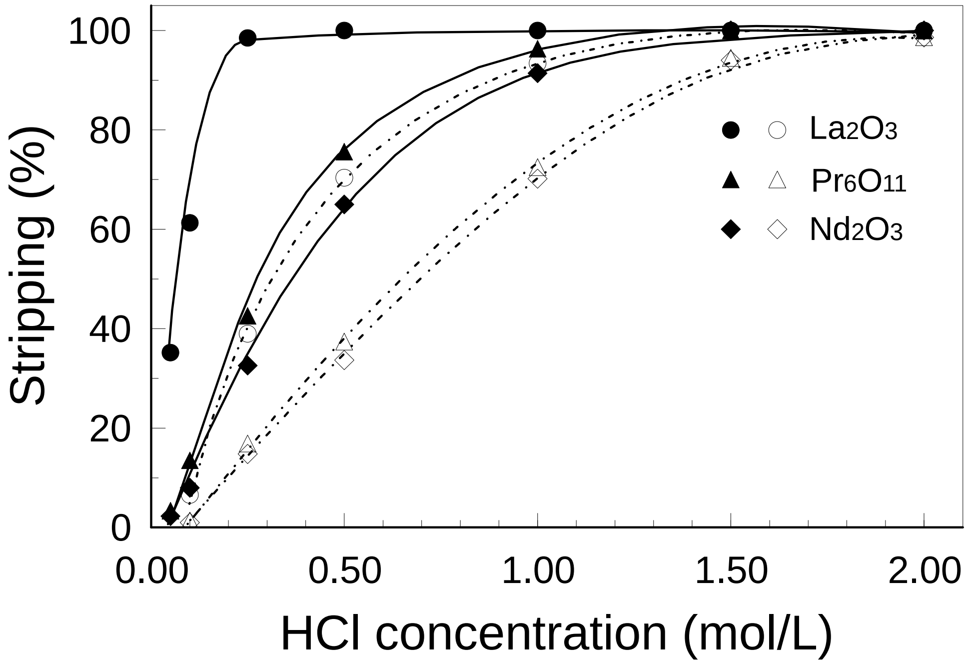


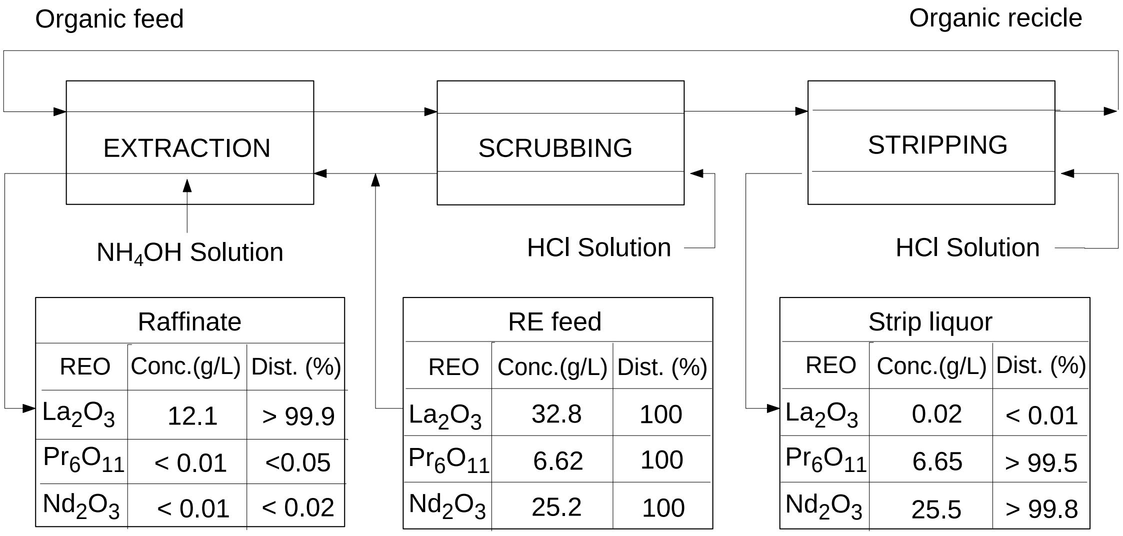
Figure 6.5. Effect of the HCl concentration on the RE elements stripping from loaded DEHPA and EHE(EHP). The dotted lines represents the experiments with DEHPA. Organic phases: HEH(EHP) - 3.41 g L^{-1} La_2O_3, 5.64 g L^{-1} Pr_6O_{11}, 24.6 g L^{-1} Nd_2O_3; DEHPA - 6.50 g L^{-1} La_2O_3, 4.92 g L^{-1} Pr_6O_{11}, 20.4 g L^{-1} Nd_2O_3.

Based upon the superior separation factor Pr/La (equal to 10.2 with HEH(EHP) and 5.4 with DEHPA), the lesser extraction of La and the easier stripping as compared to DEHPA, HEH(EHP) was selected for the experiments in a continuous mixer-settler battery.

6.3.2. Continuous Experiments

The batch experiments indicated that praseodymium and neodymium are more easily extracted than lanthanum. Then, the objective of the continuous experiments was to transfer praseodymium and neodymium to the organic phase, lanthanum being kept in the raffinate.

In the continuous experiments, the variables studies were: number of stages in the extraction, scrubbing and striping steps; organic/aqueous ratio in all steps, HCl concentration in the scrubbing and striping; NH_4OH concentration and the extraction stage were the pH was adjusted. The experimental set-up was comprised by three cycles: extraction, scrubbing and stripping (Fig. 6.6). The variables were progressively adjusted in the consecutive runs until the desired yields and grades were achieved. Figure 6.6 shows the composition and distribution of the products obtained in a continuous counter-current circuit for lanthanum recovery of the experiment leading to the best yields.



Raffinate		
REO	Conc.(g/L)	Dist. (%)
La_2O_3	12.1	> 99.9
Pr_6O_{11}	< 0.01	<0.05
Nd_2O_3	< 0.01	< 0.02

RE feed		
REO	Conc.(g/L)	Dist. (%)
La_2O_3	32.8	100
Pr_6O_{11}	6.62	100
Nd_2O_3	25.2	100

Strip liquor		
REO	Conc.(g/L)	Dist. (%)
La_2O_3	0.02	< 0.01
Pr_6O_{11}	6.65	> 99.5
Nd_2O_3	25.5	> 99.8

Figure 6.6. Composition and distribution of the products obtained in a continuous counter-current circuit for lanthanum recovery. REO = rare earth oxide, Conc. = concentration, Dist. = distribution.

The extraction occurred in the stages 1 to 8. The aqueous solution containing the rare earth elements was fed in the eighth stage, and the organic solution was fed in the first. The scrubbing solution was added in the sixteenth stage in order to achieve the selective lanthanum stripping, which was partially extracted. The pH control was made by addition of ammonium hydroxide. The ammonium hydroxide and the scrubbing solutions were combined with the RE feed solution in the raffinate, which was then removed in the first stage. The praseodymium and neodymium-loaded organic, after passing through the scrubbing stage, fed the stripping cycle, stages 17 to 22. The stripping solution was fed in the twenty-second stage and the strip liquor was removed in the stage 17. The organic effluent was filtered and recycled in the circuit without any additional treatment.

The profiles of lanthanum, praseodymium and neodymium in the aqueous phase are shown in Figure 6.7, according to the results obtained in the experiments leading to highest yields. The high efficiency of the proposed separation process is depicted in Figures 6.6 and 6.7. In the raffinate leaving the first stage, only lanthanum was detected. In the strip liquor leaving the last stage, basically only praseodymium and neodymium were observed.

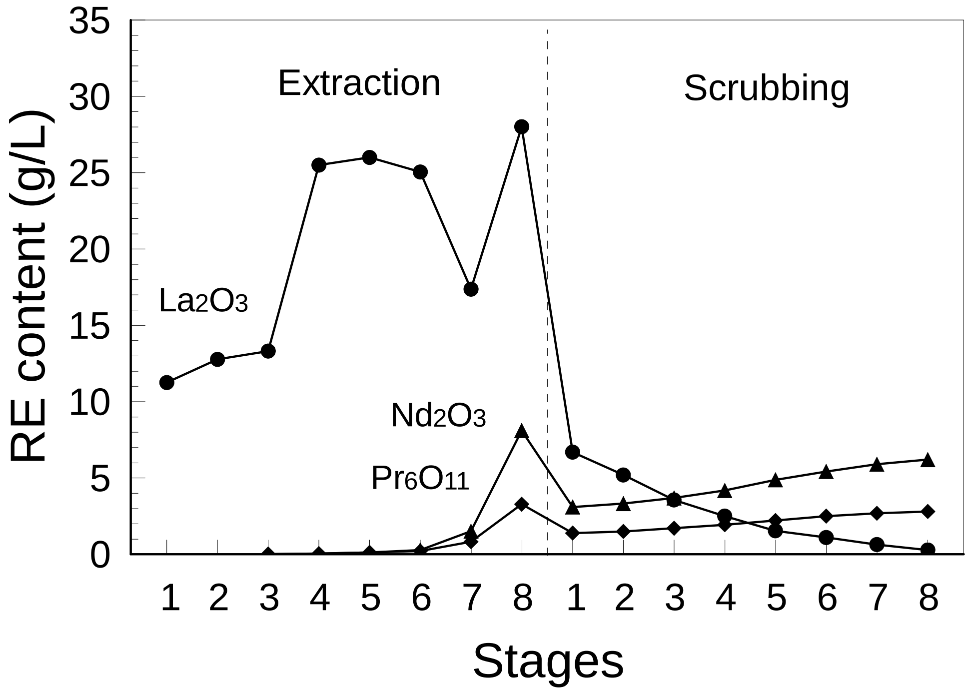


Figure 6.7. Profile of the RE elements in aqueous phase of the extraction and scrubbing circuit.

6.4. CONCLUSIONS

The use of solvent extraction to obtain high-grade, high-yield lanthanum oxide from a light rare earths mixture has been demonstrated. The process consisted in extracting Pr and Nd into 1.5 mol L^{-1} HEH(EHP) diluted in Exxsol, followed by the scrubbing of the organic phase with HCl solution and the return of the extracted La to the aqueous phase. 16 stages were required in this separation. Finally, Pr and Nd were stripped with another HCL solution in 6 stages, using an organic/aqueous phases ratio of two. A product assaying over 99.9% La_2O_3 was obtained from a chloride liquor containing 32.8 g L^{-1} La_2O_3, 6.62 g L^{-1} Pr_6O_{11} and 25.2 g L^{-1} Nd_2O_3. The overall recovery was superior to 99.9%.

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CAPÍTULO 7

CONSIDERAÇÕES FINAIS

Os estudos de recuperação do európio pela técnica de redução química, realizados com a solução pura de cloreto de európio, indicaram como variáveis mais importantes a acidez da solução de alimentação e a concentração de sulfato no recipiente onde é recolhido o európio reduzido. A acidez elevada das soluções de cloreto de terras raras de alimentação, além de reduzir a recuperação do európio, aumenta a solubilização do redutor (zinco), reduzindo a vida útil do recheio da coluna e os custos operacionais. A redução da recuperação do európio deve-se à redução de íons hidrogênio (H^+), com formação de moléculas de hidrogênio (H_2), que competem com a redução do európio (III). Quando a recuperação de európio por redução química se processa a partir de soluções contendo uma mistura de terras raras, aparece outra variável de grande importância: o nível de supersaturação, controlado a partir da taxa de adição dos íons sulfato. A adição contínua, ao propiciar a manutenção da concentração de sulfato em níveis mais baixos durante toda a operação, favorece o aumento da recuperação do európio e da pureza do produto, esta pela prevenção da co-precipitação das demais terras raras trivalentes.

Os estudos de recuperação de európio pela técnica de redução fotoquímica indicaram como principais variáveis a relação molar sulfato/európio, a relação molar ácido fórmico/európio e a concentração de terras raras totais. A concentração de terras raras totais é a variável mais crítica do processo. Isso se deve a menor solubilidade dos lantanídeos em meio sulfúrico. Esta solubilidade é ainda mais reduzida na presença de compostos orgânicos, utilizados como removedores de radical, devido ao efeito anti-solvente. A recuperação de európio a partir de soluções onde a relação terras raras totais/európio é muito elevada torna-se inviável. Isso porque, para se evitar a co-precipitação das outras terras raras trivalentes, é necessária uma maior diluição, o que resulta no aumento do volume de solução a ser tratado. A técnica de redução fotoquímica mostrou-se indicada para a recuperação de európio a partir de soluções diluídas, com baixas concentrações de outras terras raras.

O estudo de separação de Eu(III)/Gd(III) por extração por solventes indicou a dificuldade de separação, mesmo parcial, desses elementos no estado trivalente. Entre os extratantes básicos estudados, os melhores resultados foram obtidos com o Primene JM-T® em meio sulfúrico e com o Aliquat 336® na forma de nitrato, em meio nítrico. O fator de separação obtido com estes extratantes foi de 2,0. Para a realização de ensaios contínuos, o Aliquat na forma de nitrato mostrou-se o mais indicado, tendo em vista a saturação do Primene JM-T em uma única contactação. Para o estudo com extratantes ácidos, foram selecionados o DEHPA e o EHE(EHP). O EHE(EHP) apresentou algumas vantagens, como, um maior fator de separação, 1,59 para o EHE(EHP) contra 1,44 para o DEHPA, e uma reextração mais favorável.

Nos estudos de fracionamento de terras raras leves por extração por solventes, pôde-se observar o melhor desempenho do EHE(EHP), comparado ao do DEHPA, principalmente na separação do lantânio. O fator de separação obtido com o EHE(EHP) para o par La/Pr foi praticamente o dobro daquele obtido com o DEHPA (10,2 e 5,42 respectivamente). Observou-se também uma reextração bem mais favorável com o EHP(EHP). Os elevados fatores de separação obtidos para o par La/Pr devem-se principalmente à ausência do cério, que se posiciona entre estes elementos na tabela periódica. Os experimentos indicaram a semelhança dos coeficientes de extração do par Pr/Nd, o que resultou em fatores de separação próximos a 1. Em ensaios contínuos realizados com o EHE(EHP) obteve-se a separação do lantânio com recuperação e pureza de 99,9 em apenas 16 estágios de misturadores/decantadores, 8 estágios de extração e 8 estágios de lavagem.

CAPITULO 8

CONTRIBUIÇÕES ESPECÍFICAS DESTE TRABALHO

Nos últimos anos, o interesse pela obtenção dos óxidos de alta pureza de elementos terras raras tem crescido muito devido a grande variedade e importância tecnológica de suas aplicações, em especial na indústria eletrônica. O domínio das técnicas de separação desses elementos, com obtenção de produtos de alta pureza, é de vital importância para o Brasil, tendo em vista suas grandes reservas geológicas de minerais de terras raras e o crescimento da demanda interna por estes produtos. Portanto, desenvolver processos para a obtenção de óxidos de terras raras de alta pureza significa agregar valor aos nossos bens minerais e elevar a capacitação tecnológica do setor.

Os resultados apresentados nessa tese constituem uma contribuição original e significativa para a definição de processos eficientes de separação dos elementos terras raras. De acordo com a literatura, a obtenção do európio de elevado grau de pureza, a partir de misturas naturais, pela técnica de redução química, requer várias etapas de redução/precipitação. Neste trabalho, foi obtido o óxido de európio com 4 noves (99.99 % puro) em apenas duas etapas de redução/precipitação. Dentre as inovações processuais que permitiram que esses resultados fossem atingidos destacam-se a introdução da adição estagiada da solução de ácido sulfúrico na precipitação do sulfato de európio (II), bem como o controle preciso das demais variáveis de processo citadas nos artigos referentes ao assunto.

O estudo de recuperação do európio pela técnica de redução fotoquímica possibilitou o domínio da técnica bem como a identificação de seu potencial e suas limitações. Os estudos de recuperação do európio por esta técnica, citados na literatura, estão restritos à utilização de soluções muito diluídas e proporções equimolares dos constituintes. No presente trabalho, os efeitos de algumas variáveis não citados na literatura foram investigados em profundidade, a saber: relação molar removedor de radical/európio, relação molar sulfato/európio, influência da concentração de európio e de outras terras raras, além da influência do potencial de redução. Neste estudo, concluiu-se que a aplicação da técnica de redução fotoquímica para a recuperação do európio está limitada a baixas concentrações de európio e de terras raras totais na solução aquosa de alimentação.

Outra contribuição de grande importância apresentada nessa tese foi o processo desenvolvido para a separação do lantânio do par Pr/Nd. A partir dos estudos realizados foi possível desenvolver um processo relativamente simples, de fácil controle, através do qual é obtido lantânio de elevada pureza (99,9%), com um excelente rendimento.

Não foram encontradas na literatura informações a respeito da separação direta do par Eu(III)/Gd(III) sem a previa redução do európio. A partir do estudo de extração por solventes com a amostra contendo o par Eu/Gd, foram identificadas condições favoráveis a esta separação, sendo descartados alguns extratantes potencialmente indicados para a separação.

CAPÍTULO 9

SUGESTÕES PARA FUTUROS TRABALHOS

- Estudar a recuperação do európio pela técnica de redução eletroquímica, de forma a compará-la com os processos de redução química e fotoquímica.

- Estudar a purificação do gadolínio a partir da amostra de carbonato de európio e gadolínio fornecida pela INB utilizando resinas poliméricas de troca iônica, visando a obtenção de uma melhor seletividade do que aquela obtida por extração por solventes.

- Avaliar a separação do par Pr/Nd com extratantes ácidos e básicos, na presença de agentes complexantes na fase aquosa, como o ácido etilenodiaminotetraacético (EDTA) e o ácido dietilenotriaminopentaacético (DTPA) e outros que possibilitem o aumento do fator de separação do par.

- Avaliar o efeito da adição de complexantes em fase aquosa na etapa de separação do par Eu/Gd por extração por solventes.

CAPÍTULO 10

PUBLICAÇÕES RELACIONADAS AO PRESENTE TRABALHO

C.A. Morais and V.S.T. Ciminelli (1998), Recovery of Europium from a Rare Earth Chloride Solution. *Hydrometallurgy*, v. 49, p.167-177.

C.A. Morais and V.S.T. Ciminelli (2001), Recovery of Europium by Chemical Reduction of a Commercial Solution of Europium and Gadolinium Chlorides. *Hydrometallurgy*, v. 60, p.247-253.

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C.A. Morais, J.S. Benedetto and V.S.T. Ciminelli (2000), Recuperação de Európio e Ítrio a partir de tubos de televisores em cores. 55º Congresso da ABM, 24 a 28 de julho de 2000, Rio de Janeiro, RJ, Brasil, CD.

ANEXO 1

Obtenção de Európio de Alto Grau de Pureza

Trabalho apresentado no XVIII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa e I Seminário de Química de Colóides Aplicada à Tecnologia Mineral – 23 a 26 de agosto de 1998, Águas de São Pedro – SP, Brasil.

OBTENÇÃO DE EURÓPIO DE ALTO GRAU DE PUREZA(1)

Carlos Antônio de Morais(2)
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RESUMO

O trabalho apresenta os resultados do estudo de separação e purificação do európio proveniente de uma solução comercial de cloreto de terras raras médias. A metodologia empregada foi a redução química através do amálgama de zinco em dois estágios. O processo consiste na redução do Eu(III) a Eu(II), seguida da precipitação do sulfato de európio(II) em atmosfera inerte (CO_2). Para o estudo das variáveis de processo utilizou-se uma solução sintética de cloreto de európio puro. Foram investigadas a influência de variáveis como: acidez, concentração e vazão da solução de európio, concentração de mercúrio no amálgama, concentração do agente precipitante (ácido sulfúrico) e vazão de CO_2. Com base nos resultados obtidos com essa solução, foram ajustadas as melhores condições para a recuperação do európio de uma solução comercial contendo como principais constituintes 2,4g/L de Eu_2O_3, 114,4g/L de Sm_2O_3 e 64,2g/L de Gd_2O_3. Foi obtido como produto final o Eu_2O_3 com 99,4% de pureza, com um rendimento de 92%.

Palavras-Chave: purificação de európio, redução de európio, separação de terras raras

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(1) Trabalho a ser apresentado no XVII Encontro Nacional de Tratamento de Minério e Metalurgia Extrativa e I Seminário de Química de Colóides Aplicada à Tecnologia Mineral, 23 a 26 de agosto de 1998 - Águas de São Pedro-SP

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1. INTRODUÇÃO

O európio faz parte do grupo dos elementos da tabela periódica designados de terras raras (TR). As principais aplicações do Eu_2O_3 são os fotoemissores vermelho ("red phosphors") utilizados nos tubos de televisores coloridos e nas lâmpadas fluorescentes, o que representa um consumo mundial de 20-30 toneladas por ano [1].

A técnica de extração por solventes tem sido largamente utilizada na separação dos elementos de terras raras em escala industrial. As terras raras são previamente separadas por grupos através de extração, a saber: terras raras leves, médias e pesadas. Em seguida, os elementos individuais são separados e purificados, em geral, também por extração por solventes [2]. Essa separação é geralmente muito difícil devido à similaridade das propriedades químicas e físicas dos elementos adjacentes [3].

O európio, o samário e o gadolínio constituem o grupo das terras raras médias. Esses elementos são estáveis no estado trivalente, porém, o európio possui a propriedade peculiar de ser facilmente reduzido ao estado divalente. A separação do európio é usualmente realizada com base nessa propriedade. Após a redução do Eu(III) a Eu(II), este é recuperado por precipitação como sulfato de európio(II) ($EuSO_4$) insolúvel. Posteriormente, o gadolínio e o samário são separados e purificados por extração por solventes [4]. A conversão do Eu(III) a Eu(II) pode ser realizada por redução química, [5 - 7], fotoquímica [2, 8, 9] ou eletroquímica [10 - 12].

O presente trabalho enfoca a redução do európio(III) pelo amálgama de zinco usando o ácido sulfúrico (H_2SO_4) como agente precipitante. Embora essa técnica de recuperação de európio seja bastante antiga, não são disponíveis na literatura informações sobre o processo, tornando-se assim necessário um estudo mais detalhado do mesmo. Para esse estudo utilizou-se uma solução sintética de cloreto de európio puro e as condições experimentais selecionadas foram então ajustadas para uma solução comercial de cloreto de terras raras médias.

A separação do európio por essa técnica envolve a redução do Eu(III) a Eu(II) pelo zinco metálico seguida da precipitação do $EuSO_4$ em atmosfera inerte. Sendo o zinco um forte agente redutor, este é capaz de reduzir os íons H^+ a H_2:

$$2\,H^+_{(aq)} + Zn_{(s)} = Zn^{2+}_{(aq)} + H_{2(g)} \qquad Eh^0_{298K} = 0{,}76V \qquad (1)$$

Para minimizar a competição entre a reação acima e a redução do európio pelo zinco (Eq. 2), este é coberto por uma fina camada de mercúrio, resultando no amálgama de zinco, também conhecido como redutor Jones. A concentração de Hg no amálgama deve ser a menor possível, uma vez que o mercúrio não participa da reação de redução do Eu(III). Isto pode ser demonstrado pelo potencial de redução associado à reação indicada pela equação (3) [15].

$$2\,Eu^{3+}_{(aq)} + Zn_{(s)} = 2\,Eu^{2+}_{(aq)} + Zn^{2+}_{(aq)} \qquad \Delta E^0_{298K} = 0{,}33V \qquad (2)$$

$$Eu^{3+}_{(aq)} + Hg_{(l)} = Eu^{2+}_{(aq)} + Hg^{2+}_{(aq)} \qquad \Delta E^0_{298K} = -1{,}28V \qquad (3)$$

A precipitação do európio é realizada em atmosfera inerte para evitar a reoxidação do európio reduzido:

$$4\ Eu^{2+}_{(aq)} + O_{2(g)} + 4H^{+}_{(aq)} = 4\ Eu^{3+}_{(aq)} + 2\ H_2O_{(l)} \qquad \Delta E^0_{298K} = 1{,}66V \qquad (4)$$

O agente precipitante usado foi o ácido sulfúrico. A precipitação é representada pela reação:

$$Eu^{2+}_{(aq)} + HSO_4^-{}_{(aq)} = EuSO_{4(s)} + H^+_{(aq)} \qquad (5)$$

2. PARTE EXPERIMENTAL

2.1 Reagentes e Soluções

A solução sintética foi preparada a partir do óxido de európio, 99,5%, produzido pela "Rhone-Poulenc, Inc". O óxido foi dissolvido em ácido clorídrico (HCl), sendo a acidez ajustada para as condições especificadas.

A solução comercial, proveniente da extinta Nuclemon, hoje Indústrias Nucleares do Brasil - INB, foi obtida do efluente aquoso do ciclo de separação das terras raras médias e pesadas. Para se produzir uma solução mais concentrada e ajustar sua acidez, as terras raras foram inicialmente precipitadas com carbonato de sódio. Os carbonatos de terras raras foram dissolvidos em uma pequena quantidade de HCl concentrado. O volume foi ajustado com água destilada de forma a se obter uma acidez final de 0,005mol/L de HCl e uma concentração de óxidos terras raras totais (TR_2O_3) de 187,4g/L, com 2,4g/L de Eu_2O_3.

O amálgama de zinco foi preparado através da lavagem do pó de zinco metálico com granulometria entre (-1,00+0,59)mm por um minuto com solução de HCl 1,0mol/L. Após a separação da solução ácida, o sólido foi contactado por 3 minutos com uma solução de $HgCl_2$ 2,0mol/L, em quantidade variável, de modo a se obter a porcentagem de mercúrio desejada no amálgama. Finalmente, o amálgama foi lavado com água destilada e transferido para uma coluna de vidro contendo uma solução de HCl 0,001mol/L. Esse procedimento foi o mesmo adotado por Stone [13] e Hillebrand [14]. Todas as soluções foram preparadas com reagentes de grau analítico e água destilada.

2.2 Procedimento

A reação de redução ocorreu em uma coluna de vidro com 60cm de comprimento e 1,6cm de diâmetro interno, recheada com 300g de zinco amálgamado. A solução de Eu_2O_3 (200mL) foi adicionada à uma vazão de 3mL/min. Em seguida, a coluna foi lavada com uma solução de HCl 0,001mol/L até a completa remoção do európio alimentado e do zinco solúvel. Tanto a solução de európio quanto a de lavagem foram coletadas em um balão volumétrico de 3 bocas, colocado sobre um agitador magnético, contendo uma solução de ácido sulfúrico, sob atmosfera de CO_2, onde foi precipitado o sulfato de európio(II) - $EuSO_4$.

O precipitado foi filtrado em cadinho tipo Gooch, lavado com solução de sulfato de amônio 0,001mol/L, dissolvido em solução de HCl e depois precipitado como carbonato, através da adição de carbonato de sódio. Finalmente, o carbonato foi calcinado de forma a se obter o óxido (Eu_2O_3).

A recuperação foi calculada com base na concentração de európio na solução de alimentação e no filtrado. As análises foram feitas por espectrometria de energia de raios-X (Sistema Kevex).

3. RESULTADOS E DISCUSSÃO

3.1 Solução Sintética

Os efeitos dos parâmetros de processo na redução e precipitação do európio foram previamente avaliados a partir de ensaios realizados com uma solução sintética. Esses parâmetros foram a acidez, a concentração e a vazão da solução alimentação, a concentração e a quantidade relativa do agente precipitante (H_2SO_4), a vazão de CO_2, o tempo de maturação do precipitado e a concentração de mercúrio no amálgama. Investigou-se, também, a solubilização do zinco durante a redução do európio e a solubilização do $EuSO_4$ durante a lavagem do precipitado. Quando não explicitadas na figura, as condições experimentais fixadas são: solução alimentação contendo 2,5g/L de Eu_2O_3, pH 2,5, alimentada a uma vazão de 3mL/min., amálgama de zinco contendo 1,0% de Hg, 30ml de solução de H_2SO_4 2,0mol/L, vazão de CO_2 de 120mL/min. e tempo de maturação do precipitado de 3 horas. O erro experimental, determinado através de replicas aleatórias dos ensaios foi de aproximadamente 3% para um nivel de confiança de 95%.

3.1.1 *Vazão da Solução Alimentação*

A vazão da solução alimentação foi estudada no intervalo de 1 a 5mL/min. Nessa faixa não foi observada uma influência significativa da variável na recuperação do óxido, conforme ilustra a figura 1, apresentada a seguir. Vazões superiores a 5mL/min. resultaram na necessidade de recondicionamento freqüente do leito. Nos ensaios subsequentes utilizou-se uma vazão de 3mL por minuto. A vazão da solução alimentação depende essencialmente das caracteristicas da coluna e da concentração da solução alimentação. Cooley e Yost [16], em estudo semelhante, usaram uma vazão de 2mL/min, enquanto McCoy [7] e Hillebrand *et al.* [14] trabalharam com vazões superiores a 30mL/min.

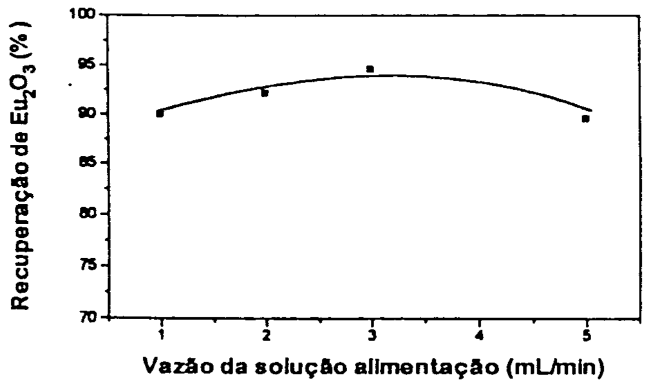

Figura 1: Influência da vazão da solução alimentação na recuperação de Eu_2O_3.

3.1.2 *Concentração de Eu_2O_3 na solução alimentação*

O aumento da concentração de európio na solução alimentação, no intervalo de 0,5 a 5,0g/L, levou a um aumento na recuperação de Eu_2O_3. A concentração de európio no filtrado permaneceu constante no nível de 0,10g/L de Eu_2O_3 (figura 2). Os resultados obtidos demonstraram a vantagem de se trabalhar com soluções mais concentradas.

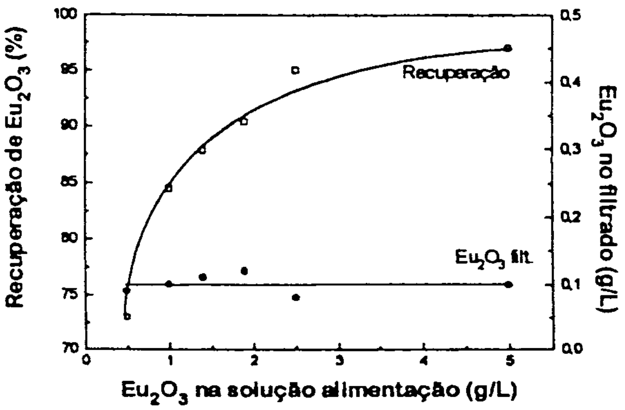

Figura 2: Correlação entre a recuperação do óxido e o európio remanescente em solução em função da concentração de európio na solução alimentação.

3.1.3 *Acidez da Solução Alimentação*

A acidez da solução alimentação foi estudada na faixa de 0,001 a 0,100mol/L de HCl. Observou-se que a acidez afeta diretamente a redução do európio. O aumento da acidez diminui a recuperação do európio e aumenta a solubilização do zinco. Isto se deve ao favorecimento da reação de formação de H_2 (Eq. 1), diminuindo assim a eficiência e a durabilidade do redutor. Não foram investigados níveis de acidez inferiores a 0,001mol/L de HCl, devido à baixa solubilidade do Eu_2O_3 em pH > 3,0. A influência da acidez na recuperação do európio e na solubilização do zinco está apresentada na figura 3.

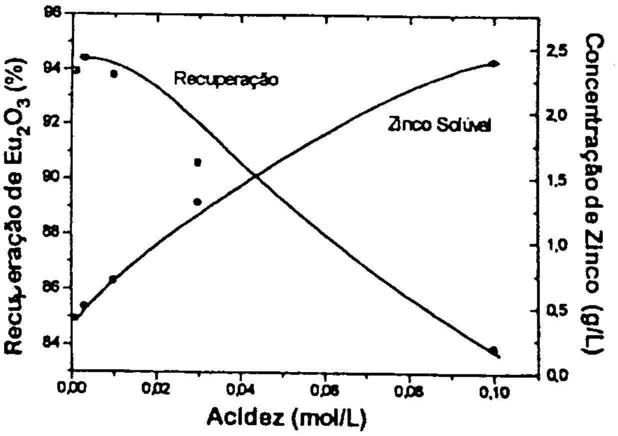

Figura 3: Influência da acidez da solução alimentação na recuperação do európio e na solubilização do zinco.

3.1.4 *Concentração de mercúrio no amálgama de zinco*

Segundo Stone [13], a concentração de mercúrio no amálgama pode variar de 0,1 a 10%, ressaltando que o amálgama ideal é aquele para o qual se obtém uma redução rápida e completa com o mínimo possível de liberação de H_2. Por isto, na escolha da concentração de mercúrio deve-se levar em consideração a natureza do oxidante e a acidez da solução que contém o metal a ser reduzido. Quando o oxidante é reduzido tanto pelo zinco como pelo mercúrio pode-se usar concentrações mais elevadas de mercúrio no amálgama. Para soluções mais ácidas, também são recomendadas concentrações maiores de mercúrio, porém se o mercúrio não participa da reação de redução a eficiência do redutor será menor. Os resultados obtidos no presente trabalho indicaram que concentrações de 1,0 e 0,5% de Hg não afetam, de forma significativa, a recuperação do európio e a solubilização do zinco.

3.1.5 *Vazão de CO_2*

Sendo o Eu(II) facilmente oxidado (Eq. 4), é necessário manter o recipiente onde a solução contendo Eu(II) é recolhida sob atmosfera inerte. Isto pode ser feito via injeção de gás carbônico (CO_2) ou de nitrogênio gasoso (N_2). Segundo McCoy [6], mesmo em atmosfera de CO_2, cerca de 1% do Eu(II) é reoxidado a Eu(III). Nesse estudo foi utilizado gás carbônico para manter a atmosfera inerte no recipiente onde ocorria a precipitação. Não foi observado nenhum efeito significativo da vazão de CO_2, no intervalo de 25 a 300mL/min., na recuperação do európio.

3.1.6 *Concentração de H_2SO_4*

O ácido sulfúrico foi utilizado como fonte de sulfato para a precipitação do $EuSO_4$. Variou-se a concentração da solução no intervalo de 0,25 a 5,0mol/L de H_2SO_4. O volume desta solução foi mantido em 30mL, o mínimo necessário para manter os tubos de entrada da solução contendo Eu(II) e do CO_2 submersos. Os resultados do estudo dessa variável estão apresentados na figura 4. Pode-se observar que a recuperação de európio aumenta levemente com o aumento da concentração de H_2SO_4 até 2,0mol/L.

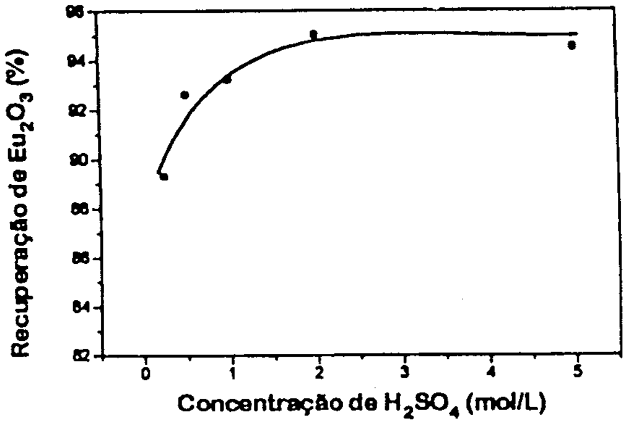

Figura 4: Influência da concentração do H_2SO_4 na recuperação de európio (solução sintética).

3.1.7 *Tempo de maturação do precipitado*

Verificou-se, durante os ensaios, que eram necessárias 3 horas para se obter uma solução límpida, livre de sólidos em suspensão. Foram feitos ensaios com tempo de maturação de 3 e 5 horas. Não houve alteração nos resultados em termos da recuperação de európio.

3.1.8 *Lavagem do $EuSO_4$*

A solubilização do precipitado de $EuSO_4$ durante a etapa de lavagem foi investigada. Nesse estudo utilizou-se água destilada, soluções de H_2SO_4 e soluções de $(NH_4)_2SO_4$. O melhor resultado foi obtido com a solução de $(NH_4)_2SO_4$ 0,001mol/L. Nesse caso, a solubilização foi de 0,01g/L de Eu_2O_3. Para a água e a solução de H_2SO_4 0,001mol/L, a solubilização foi respectivamente de 0,09g/L e 0,12g/L de Eu_2O_3. Foram utilizados 50mL de cada uma das soluções.

3.2 Solução Comercial

Conforme observado nos ensaios realizados com a solução sintética, as variáveis que mais afetaram a recuperação de európio foram a acidez e concentração da solução alimentação e a concentração de ácido sulfúrico no recipiente de precipitação. Dessa forma, a solução comercial foi concentrada e a acidez ajustada para valores próximos aos da solução sintética. Obteve-se, assim, uma solução com acidez de 0,005mol/L de HCl (pH 2,3), contendo 2,4g/L de Eu_2O_3. Uma concentração maior de európio comprometeria a acidez da solução devido ao alto teor de samário e gadolínio. A concentração de terras raras totais na solução ficou em 187,4g/L de TR_2O_3. A composição dessa solução está apresentada na Tabela 1.

Tabela 1: Composição da solução alimentação

TR_2O_3	Composição	
	g/L	%
La_2O_3	<0.02	<0.002
Ce_2O_3	<0.02	<0.002
Pr_6O_{11}	<0.02	<0.002
Nd_2O_3	0.81	0.07
Sm_2O_3	114.4	9.29
Eu_2O_3	2.40	0.19
Gd_2O_3	64.2	5.21
Tb_4O_7	4.10	0.33
Y_2O_3	1.45	0.12

Densidade: 1,232g/cm^3

As condições selecionadas para os ensaios foram: alimentação a uma vazão de 3mL/min., amálgama de zinco contendo 1,0% de Hg, 30ml de solução de H_2SO_4 2,0mol/L, vazão de CO_2 de 120mL/min. e tempo de maturação do precipitado de 3 horas.

O resultado obtido foi muito aquém do esperado. Obteve-se uma recuperação de apenas 63%, enquanto que para a solução sintética foi obtida uma recuperação de

95%. Fez-se então um novo estudo da influência do agente precipitante, variando-se a concentração e o volume da solução de H_2SO_4. A concentração foi estudada no intervalo de 2,0 a 7,0mol/L de H_2SO_4 com 30 e 60mL dessa solução. As demais variáveis foram mantidas nos níveis selecionados anteriormente. O melhor resultado foi obtido na concentração de 3,5mol/L de H_2SO_4, quando obteve-se uma recuperação de Eu_2O_3 de 92%, com pureza de 92,2%. Esses resultados estão apresentados nas figuras 5a e 5b.

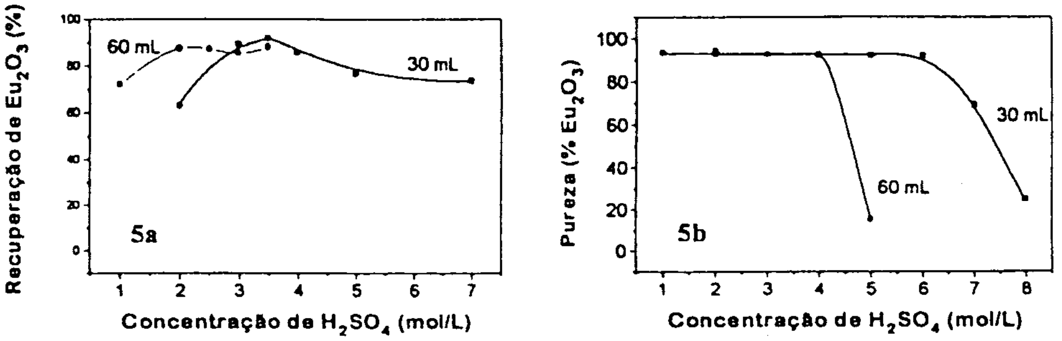

Figura 5: Influência da concentração e do volume da solução de H_2SO_4 na recuperação (5a) e pureza (5b) do európio obtido. Solução alimentação: pH 2,3 contendo 2,4g/L de Eu_2O_3.

Após a realização desses ensaios, observou-se que não era possível a obtenção de európio de alto grau de pureza em apenas um estágio do processo. A purificação do produto foi estudada a partir da solução preparada com o precipitado obtido na melhor condição da etapa anterior.

3.2.1 *Estágio de Purificação*

O precipitado de európio obtido no primeiro estágio (estágio de separação) foi dissolvido em HCl de forma a se obter uma solução contendo 5,5g/L de Eu_2O_3 em uma acidez de 0,001mol/L de HCl. O comportamento dessa solução na etapa de precipitação foi semelhante ao da solução sintética. Dessa forma, a concentração do agente precipitante foi mantida em 0,5mol/L de H_2SO_4 para evitar maior contaminação do produto, em conseqüência da co-precipitação do Sm e Gd. As demais condições foram mantidas as mesmas do primeiro estágio. Nesse segundo estágio, foi obtido um produto com 99,4% de Eu_2O_3, sendo a recuperação de 97%. As composições da solução intermediária e do produto final estão apresentadas na Tabela 2, a seguir.

Tabela 2: Composição da solução intermediária e do produto final

TR_2O_3	AMOSTRA	
	Sol. intermediária (g/L)	Produto final -Eu_2O_3 (%)
La_2O_3	< 0.02	0.03
Ce_2O_3	< 0.02	0.02
Pr_6O_{11}	< 0.02	0.01
Nd_2O_3	0.02	0.04
Sm_2O_3	0.40	0.40
Eu_2O_3	5.50	99.4
Gd_2O_3	0.06	0.03
Tb_4O_7	< 0.02	< 0.03
Y_2O_3	< 0.02	< 0.03

4. CONCLUSÃO

Nos níveis estudados, a recuperação do európio foi afetada principalmente pela acidez e concentração do metal na solução e pela concentração de ácido sulfúrico no recipiente de precipitação do $EuSO_4$. Foi obtido um produto com 99,4% de Eu_2O_3 partindo de uma solução contendo 2,4g/L de Eu_2O_3. A recuperação do metal foi de aproximadamente 92%, desconsiderando o possível reciclo do efluente. Um produto com pureza mais elevada pode ser obtido através da adição de um maior número de estágios de purificação e de uma melhor separação das terras raras leves e pesadas nos estágios de extração por solventes.

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OBTAINING OF HIGH PURITY EUROPIUM OXIDE

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Raquel Maia Mingote
Virginia Sampaio T. Ciminelli

ABSTRACT

The separation and purification of europium from a commercial rare earth chloride solution was investigated. The process consisted in the reduction of Eu(III) to Eu(II) by zinc amalgam, followed by the precipitation of europium(II) sulphate ($EuSO_4$) in an inert atmosphere (CO_2). The influence of variables such as acidity, concentration and flow rate of the rare earth chloride solution, mercury concentration in the zinc amalgam, concentration of the precipitating agent (sulphuric acid), and the CO_2 flow rate, have been evaluated with pure europium synthetic solution. Based on the results, the experimental conditions have been adjusted to recover europium from a commercial rare earth solution, containing 2.4g/L Eu_2O_3, 114.4g/L Sm_2O_3 and 64.2g/L Gd_2O_3 as the main constituents. A final product, assaying 99.4% Eu_2O_3, was obtained with a recovery of 92%.

Key-words: europium reduction, europium purification, rare earth separation.

ANEXO 2

Recuperação de Európio e Ítrio a Partir de Tubos de Televisores em Cores

Trabalho apresentado no 55º Congresso da ABM - 24 a 28 de julho de 2000, Rio de Janeiro, RJ, Brasil.

RECUPERAÇÃO DE EURÓPIO E ÍTRIO A PARTIR DE TUBOS DE TELEVISORES EM CORES[1]

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RESUMO

Este trabalho apresenta os resultados do estudo de separação de európio e ítrio em uma solução sulfúrica obtida a partir da lixiviação de rejeitos constituídos de pó de revestimento de tubos de televisores em cores. Primeiramente foi realizado um estudo de lixiviação do pó, seguido da recuperação de európio e ítrio, utilizando a técnica de extração por solventes. Os resultados obtidos indicam a viabilidade técnica de utilização do processo desenvolvido para recuperação destes metais com alto grau de pureza. No processo de lixiviação foi obtido uma recuperação de 95% e 90% para o ítrio e európio, respectivamente. No processo de extração por solventes, obteve-se um fator de separação destes metais superior a 9, que é considerado uma ótima condição de separação.

Palavras-chave: recuperação de európio, recuperação de ítrio, televisores em cores.

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1. INTRODUÇÃO

Os tubos dos televisores em cores possui como revestimento da tela uma mistura de óxidos que contém quantidade significativa de európio e ítrio, dois elementos da série dos lantanídeos, que têm alto valor comercial. O európio em combinação com o ítrio, é responsável pela cor vermelha no televisor. Os monitores de computadores utilizam o mesmo princípio. Algumas outras aplicações destes elementos são, no caso do európio, telas de raio-X, lâmpadas fluorescentes, cintiladores de neutrons, memória de sistemas de leitura ótica. O ítrio é utilizado em produção de laser, filtros de microondas, produtos magnéticos e absorvedores de neutrons[1,2]. A separação destes elementos possibilita a utilização dos mesmos em outras aplicações, aumentando assim o valor agregado destes.

Os minérios de terras raras, como monazita e xenotina, são muito resistentes a ataques químico. A abertura destes minerais geralmente é realizada à altas temperaturas com ácido sulfúrico concentrado (H_2SO_4 93% p/v, 210^{o}C) ou hidróxido de sódio (NaOH 70% p/v, 150^{o}C) [3,4]. Porém, a abertura de seus óxidos já é possível com outros ácidos minerais e em condições mais suaves [5].

A separação dos terras raras adjacentes é geralmente muito difícil devido a semelhança de suas propriedades [6]. O ítrio, porém, apresenta comportamento mais similar aos lantanídeos de número atômico mais elevado (67, 68), pertencentes ao grupo das terras raras pesadas [7,8,9]. O fato do európio, com número atômico 63, pertencer ao grupo das terras raras médias, torna a separação európio/ítrio mais fácil. Esta separação pode ser realizada por troca iônica [10] ou por extração por solventes [11]. Os extratantes mais utilizados na extração de terras raras são os organofosfóricos, destacando-se o ácido di (2-etilhexil) fosfórico (DEHPA) [8,11,12]. Outra classe de extratante também utilizada é das aminas [9,13,14].

Este trabalho envolveu uma etapa de lixiviação seletiva dos elementos de interesse e uma etapa de extração por solventes. No estudo de lixiviação foi investigado o tipo de ácido (HCl e H_2SO_4), a relação ácido/sólido, a temperatura e o tempo de lixiviação. O estudo de separação do európio e ítrio foi realizado utilizando a técnica de extração por solventes. Esse processo é, em geral, aplicado quando se deseja a separação de um determinado metal ou composto com elevado nível de pureza, isto por ser altamente seletivo. Baseado nesse fato, essa técnica foi aplicada para o sistema em estudo, com o objetivo de separar o európio (Eu) e ítrio (Y) dos demais componentes presentes na mistura. O processo apresenta basicamente três etapas: extração, reextração e regeneração do solvente. Na etapa de extração as variáveis estudadas foram: tipo e concentração do extratante (DEHPA e Primene JM-T), acidez da fase aquosa de alimentação, cinética de extração e relação de fases. Na etapa de reextração investigou-se o tipo e concentração do ácido e a relação volumétrica entre as fases orgânica e aquosa.

2. TRABALHO EXPERIMENTAL

2.1 Reagentes e soluções

Uma amostra de 1 kg, contendo európio e ítrio, foi obtida a partir de sucata de telas de televisores em cores. No estudo de lixiviação utilizou-se os ácidos clorídrico (HCl) e sulfúrico (H_2SO_4). Os reagentes utilizados na etapa de extração foram:

Primene JM-T, uma amina primária, fornecido pela Rohm and Haas Química Ltda, e o ácido di (2-etilhexil) fosfórico (DEHPA), fornecido pela Albright & Wilson Americas, Inc., como extratantes. Como solvente foi utilizado o Exxsol (querosene purificado), fornecido pela Exxon Química Ltda. No caso do Primene foi utilizado o tridecanol, como modificador. Na etapa de reextração utilizou-se soluções de ácido clorídrico e sulfúrico. Todas as soluções aquosas foram preparadas com reagentes de grau analítico e água destilada.

2.2 Procedimento

A amostra de ítrio e európio foi inicialmente homogeneizada e quarteada em alíquotas de 20 gramas para a caracterização química e realização dos ensaios de lixiviação. Estes foram realizados em bequer de 250 mL, imersos em banho-maria, com temperatura controlada, conforme a condição do experimento e agitação mecânica com hélice de vidro.

Os ensaios de extração e reextração foram realizados em bequer de 100 mL, também com agitação mecânica. Após concluído o tempo de contactação, a mistura era transportada para um funil de separação, para processar-se a separação das fases.

As análises de európio e ítrio foram realizadas por espectrometria de energia de raios-X (sistema Kevex); os demais elementos foram determinados por espectrofotometria de absorção atômica. O erro experimental, determinado através de replicas aleatórias dos ensaios foi de aproximadamente 5%, para um nível de confiança de 95%.

3. RESULTADOS E DISCUSSÃO

3.1 Lixiviação

A tabela 1 apresenta a caracterização química dos principais constituintes da amostra estudada. Observa-se que os teores de európio e ítrio são bastante significativos, principalmente quando comparado às concentrações destes elementos nas matrizes minerais de onde são originados (por exemplo: monazita- em torno de 0,1% Eu_2O_3 e 2,0% Y_2O_3) [15].

TABELA 1 : Caracterização química dos principais constituintes da amostra

Óxido	Y_2O_3	Eu_2O_3	CdO	ZnO	S	$BaSO_4$	PbO	Fe_2O_3	SrO	Sb_2O_4	ZrO_2
Teor (%)	6,0	0,38	3,5	31,7	20,0	3,5	3,0	2,63	1,2	0,20	0,17

Outro constituinte que aparece em grande teor na amostra é o silício (27,8% SiO_2). Porém grande parte deste é proveniente do vidro do televisor, não fazendo assim, parte da composição do pó de revestimento do tubo. O teor de silício encontrado em uma outra amostra obtida com mais critério foi de 3,14% SiO_2.

Ensaios preliminares de lixiviação foram feitos utilizando-se ácido clorídrico e ácido sulfúrico, variando-se a relação ácido/sólido e mantendo-se constantes as demais condições de processo. Os resultados destes experimentos estão apresentados nas figuras 1a e 1b. Nestas figuras é apresentado também o comportamento de lixiviação do cádmio, outro elemento de elevado valor comercial que aparece em teor razoável na amostra. O ácido sulfúrico foi mais eficaz e seletivo na lixiviação de európio e ítrio, sendo, portanto selecionado como o agente de lixiviação. Observa-se, por outro lado, a seletividade do ácido clorídrico em relação ao cádmio, o que abre uma possibilidade de separação seletiva do metal. Estudos do tempo de lixiviação indicaram que duas horas são suficientes para se atingir níveis satisfatórios de solubilização dos elementos de interesse, sendo este o tempo utilizado nos ensaios subsequente.

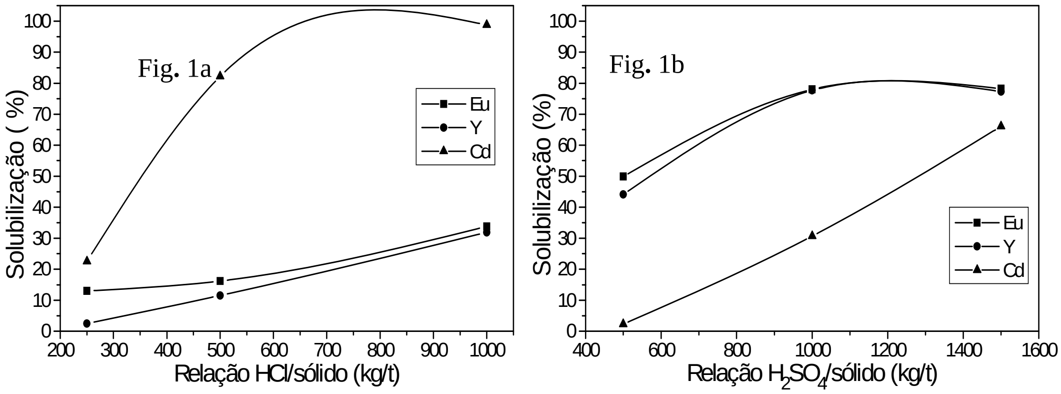

FIGURA 1: Solubilização de európio, ítrio e cádmio nos ensaios de lixiviação clorídrica (Fig.1a) e sulfúrica (Fig.1b). *70^{o}C, 2:00h, 40% de sólidos.*

Para avaliar o efeito da temperatura, foram realizados ensaios à temperatura ambiente (27^{o}C), 70^{o}C e 90^{o}C. O rendimento de solubilização do európio e ítrio cresce significativamente com o aumento da temperatura. A figura 2 mostra a influência da temperatura (70 e 90 ^{o}C) em função de relação ácido/sólido. Pode-se observar que a 90^{o}C a relação H_2SO_4/sólido pouco influencia na solubilização de európio e ítrio.

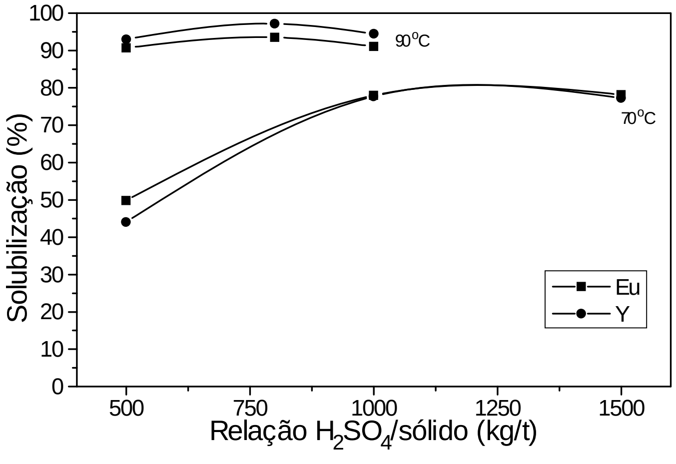

FIGURA 2: Influência da temperatura na solubilização de európio e ítrio em função da relação ácido/sólido. *2:00h, 40% de sólidos.*

3.2 Extração

Os ensaios de extração foram realizados utilizando a solução sulfúrica proveniente da etapa de lixiviação, mantendo uma relação H_2SO_4/sólido de 500 kg/t, a 90ºC. A caracterização química desse licor é apresentada na tabela 2.

TABELA 2: Caracterização da Lixívia Sulfúrica

Constituinte	Y_2O_3	Eu_2O_3	CdO	ZnO	Fe_2O_3	SO_4^{2-}
Teor (g/L)	7,73	0,41	0,11	6,60	6,22	130

pH = 0,3

Foram investigados dois extratantes para separação dos elementos európio e ítrio em meio sulfúrico: uma amina primária (Primene JMT) e um ácido organofosfórico (DEHPA). Em todos os ensaios realizados com o Primene JMT, utilizou-se 10% de tridecanol, com a finalidade de aumentar a solubilidade da espécie extraída, evitando-se assim a formação de uma terceira fase. A tabela 3 apresenta os resultados preliminares realizados com esta amostra utilizando os agentes de extração mencionados, com ajuste de pH da lixívia sulfúrica.

TABELA 3: Influência do pH na extração de Eu, Y, Fe, Cd e Zn com Primene e DEHPA

pH	Extração (%)									
	Primene					DEHPA				
	Eu_2O_3	Y_2O_3	Fe_2O_3	CdO	ZnO	Eu_2O_3	Y_2O_3	Fe_2O_3	CdO	ZnO
0,3	61,0	31,2	2,99	<0,01	1,54	4,68	74,0	2,45	<0,01	1,24
0,9	86,8	64,4	7,36	<0,01	1,04	4,89	76,2	2,53	<0,01	1,52
1,2	86,6	71,4	8,51	<0,01	0,97	-	-	-	-	-
1,6	-	-	-	-	-	5,56	84,5	2,99	<0,01	2,22

Condições: Primene JMT 20% (V/V), DEHPA 20% (V/V); 5 min de contactação, O/A=1

Através destes ensaios, observou-se uma influência maior do pH quando o Primene foi utilizado como extratante. Neste caso, o rendimento de extração dos elementos európio, ítrio e ferro aumentam significativamente com o aumento do pH. Em pH 1,6 ocorreu formação de emulsão. Para o DEHPA, a variação do rendimento de extração com o pH foi muito pequena comparada ao Primene. Embora o DEHPA tenha apresentado maior seletividade na extração do ítrio, a utilização deste extratante foi abandonada devido à formação de uma camada de micela na interface de contato entre as fases aquosa e orgânica em toda faixa de pH estudada. A concentração de Primene foi estudada no intervalo de 10 a 40% (V/V). Os resultados estão apresentados na figura 3. Nestes ensaios, o pH da solução aquosa foi mantido em 0,3; a relação de fases O/A igual a 1 e o tempo de contactação de 5 minutos.

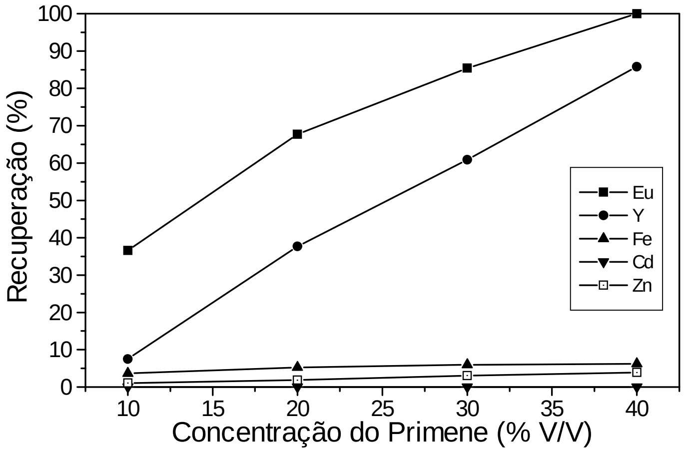

FIGURA 3: Influência da concentração de Primene na extração de Eu, Y, Fe, Cd e Zn. *Tempo de contactação=5 min, O/A=1, pH =0,3.*

Conforme esperado, a extração de európio e ítrio aumenta com o aumento da concentração do extratante. Nestas condições, os níveis de extração de ferro e zinco mantêm- se em torno de 6% e 3% respectivamente, enquanto o cádmio não é extraído.

A acidez da solução de alimentação é um parâmetro que exerce uma influência bastante significativa no processo de extração, conforme observado na tabela 3. Para a faixa de pH estudada (0,3 a 1,2), observa-se (figura 4) que a extração de európio atinge um máximo a partir do pH igual a 0,6, enquanto que a recuperação de ítrio continua crescente com o pH.

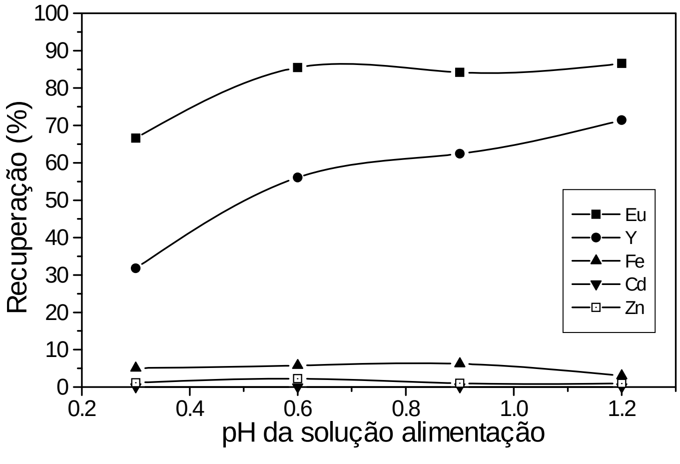

FIGURA 4: Influência do pH na extração de Eu, Y, Fe, Cd e Zn com Primene. *Conc. Primene=20% V/V, Tempo de contactação=5min, O/A=1.*

O tempo de contactação foi investigado no intervalo de 1 a 10 minutos. A cinética de extração foi extremamente elevada, sendo observado que um minuto é suficiente para que o sistema atinja o equilíbrio. Outra variável estudada na etapa de extração foi a relação volumétrica das fases orgânica e aquosa. A medida que se aumenta a relação orgânico/aquoso (O/A), o fator de separação do par európio/ítrio diminui. A extração dos demais elementos é mantida nos níveis anteriormente observados (fig. 5).

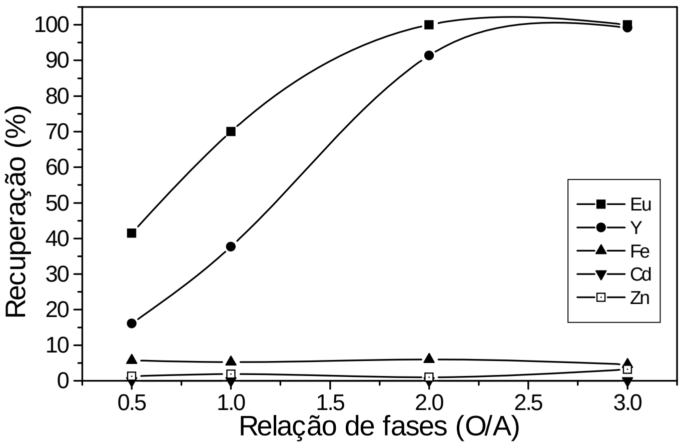

FIGURA 5: Influência da relação de fases O/A na extração de Eu, Y, Fe, Cd e Zn. *Conc. Primene = 20% V/V, Tempo de Contactação=5 min, pH = 0,3.*

3.3 Reextração

A obtenção dos elementos európio e ítrio isolados pode ser alcançada na etapa de reextração ácida. Para isso, foi investigada a eficiência da reextração destes metais presentes no extrato orgânico utilizando-se os ácidos clorídrico e sulfúrico. A caracterização dos principais constituintes presentes na solução orgânica carregada, com a qual foram realizados os ensaios de reextração, é apresentada na tabela 4.

TABELA 4: Caracterização da Solução Orgânica Carregada

Óxido	Y_2O_3	Eu_2O_3	CdO	ZnO	Fe_2O_3
Teor (g/L)	7,16	0,39	<0,05	0,08	0,33

Na figura 6 são apresentadas as curvas de recuperação de európio e ítrio em função da concentração de ácido clorídrico (Figura 6a) e de ácido sulfúrico (Figura 6b). Nesta etapa ocorre a reextração preferencial do ítrio. Em ambos os meios, como era de se esperar, a reextração destes elementos aumenta com o aumento da concentração do ácido, sendo que a melhor condição de separação do par európio/ítrio ocorre nas concentrações abaixo de 0,25mol/L, onde não foi observado a reextração de ítrio, porém, nesta faixa de acidez o rendimento de reextração de európio é muito baixa, sendo necessário um número grande de estágios. Outra possibilidade de separação seria a reextração com uma solução mais ácida (1,0 mol/L) conjugada com a etapa de extração.

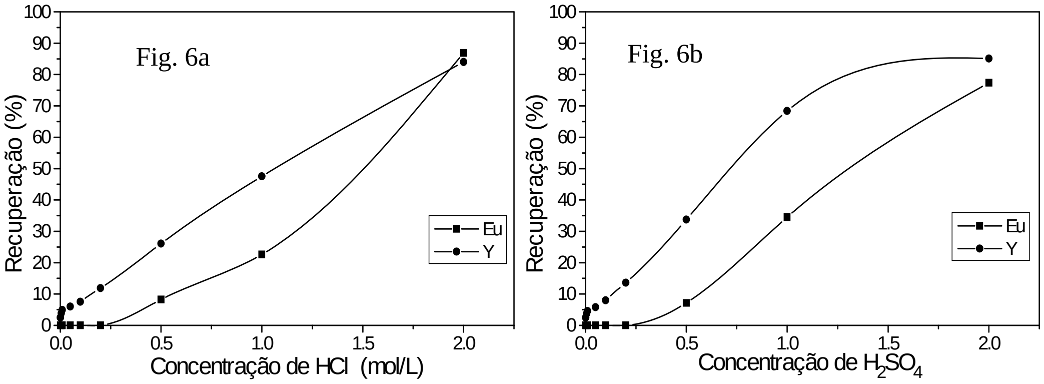

FIGURA 6: Influência da concentração do ácido clorídrico (Fig. 6a) e sulfúrico (Fig 6b) na reextração de európio e ítrio. *Tempo de contactação=5min, O/A=3.*

Ensaios variando a relação entre as fases orgânica e aquosa (O/A) no intervalo de 1 a 5 (V/V) utilizando H_2SO_4 1,0 mol/L como reextratante não indicaram alteração significativa no fator de separação do par Eu/Y.

4. CONCLUSÕES

A amostra de pó metálico coletada nos tubos de TV possui teor significativo de európio e ítrio. A recuperação destes metais isolados é possível com aplicação dos processos de lixiviação ácida seguida de extração por solventes. O ácido sulfúrico mostrou-se mais eficiente na lixiviação do európio e ítrio, com recuperação de 90 e 95%, respectivamente. Na etapa de extração, o Primene JM-T apresentou melhor desempenho que o DEHPA. A reextração seletiva de Eu/Y pode ser realizada tanto com ácido clorídrico quanto com ácido sulfúrico. A confirmação do processo deve ser feita através de ensaios contínuos.

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RECOVERY OF EUROPIUM AND YTTRIUM FROM COLOR TV TUBES [1]

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ABSTRACT

This paper presents the results of a study on the separation of europium and yttrium from a sulfuric solution obtained from leaching the coating powder of useless color TV tubes. First of all it was carried out a leaching study of the powder, followed by the recovery of europium and yttrium, using the solvent extraction technique. The results showed that the developed process can be used for the recovery of these metals with a high degree of purity. The leaching step recovery reached of 95% for yttrium and 90% for europium. On the solvent extraction step a metal separation factor higher than 9 was obtained.

Key words: europium recovery, yttrium recovery, color tv

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