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Abstract

A processing scheme for the caldasite, a mixture of zircon and baddeleyite abundant in the Poços de Caldas Plateau, has been investigated aiming at a joint recovery of the uranium and zirconium values of the ore. The uranium - zirconium and iron - zirconium separations were done by precipitation of basic zirconium sulphates. The uranium was recovered by extraction of the mother liquor from the first zirconium precipitation by employing Alamine 336 in an inert diluent. End products are sodium diuranate and a commercial grade of zirconium oxide. Estimated production costs compared favourably with Brazilian import prices.

INTRODUCTION

The widespread occurrence of uranium in the zirconium ores of the Poços de Caldas Plateau in the State of Minas Gerais has been known for quite a number of years, but only recently has the interest on these ores been revived. The so-called caldasite, a mixture of zircon and baddeleyite abundant in the plateau, has an average uranium content of 0.30% U_3O_8 and zirconium contents higher than 70% ZrO_2. However, this ore is rather refractory to conventional acid leaching procedures. Sulphuric acid leaching yields less than 5% uranium recovery. Large efforts were expended in the past in searching for adequate recovery techniques for its uranium values [1], until it was finally decided to process the ore mainly for its zirconium content and recover the uranium as a by - product.

The scattered occurrence of the hydrothermal ore - bodies in the plateau led to erroneous estimates of the total caldasite reserves in the past, but it is reasonably well known today in addition to the 22 000 ton lot in storage on the premises of the Brazilian CNEN field works in the plateau, there is about 100 000 ton of unexplored ore averaging 0.30% U_3O_8 and 60% ZrO_2. More recent discoveries of additional deposits of a lower grade ore, amenable to physical concentration, increased the unexplored reserves two - fold. Therefore, it is conservatively estimated at the present (mid 1970) that the uranium and zirconium reserves may reach up to 667 ton U_3O_8 and 133 500 ton ZrO_2, respectively. A typical analysis of the ore is given in Table I.

The processing scheme to be described in the paper aims at the joint recovery of the uranium and zirconium values of the ore. However, due to the very nature of the ore, more emphasis was placed on the zirconium recovery as a commercial grade oxide.

TABLE I
TYPICAL ANALYSIS OF THE CALDASITE

Component	U_3O_8	ZrO_2	HfO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	SiO_2
Content (%)	0.32	61.2	0.9	0.65	3.0	7.7	0.30	22.1

PROCESSING SCHEME

The fundamental problems in processing the caldasite are the chemical opening of the ore, the uranium - zirconium separation and the iron - zirconium separation. Several processes were attempted in the past in the opening of the ore, such as hot H_2SO_4 curing and digestion [1,2], concentrated HNO_3 digestion [3], fusion with $KHSO_4$ [1], $NaHSO_4$ [3], Na_2CO_3 [3], NaOH [1,3,4], NaOH + $NaNO_3$ [1], NaOH + NaCl [1] and NaOH + NaF [1,5]. The larger par of the efforts were of no avail. However, the NaOH fusion, or even better the NaOH + NaF fusion, when properly conducted yields nearly 100% uranium recoveries and over 97% recovery of the zirconium. The fused mass, analogously to the usual process for zircon concentrates, can be treated by hot digestion with mineral acids to dissolve the uranium and zirconium contents. The uranium - zirconium and iron - zirconium separations can be done by a variety of different processes.

The processing scheme about to be discussed consists mainly of the following group of unit processes: (1) NaOH fusion of the ore followed by leaching with hot water, sulphuric acid digestion and separation of most of the zirconium by precipitation as a basic zirconium sulphate, (2) processing the precipitated sulphates to eliminate insoluble products and accompanying impurities to produce a commercial grade of zirconium oxide, and (3) recovery of the uranium values by solvent extraction of the mother liquor from the basic zirconium sulphate precipitation.

Alkaline fusion and uranium - zirconium separation

Opening the ore is a critical operation from an economic standpoint, because it charges considerably production costs. For this reason a search for optimized conditions for this process was done by the steepest - ascent procedure employing data from a complete factorial design on the variables time, temperature and NaOH/ore ratio. An optimized condition for over 97% zirconium recovery and nearly 100% uranium recovery was found around the point:

time = 1.52 ± 0.09 hour
temperature = 805 ± 15°C
NaOH/ore ratio = 1.7 ton/ton.

Under these conditions, excess NaOH over the stoichiometric equivalent of the ore amounts to almost 25%. The alkaline fusion and subsequent processes up to the precipitation of basic zirconium sulphates are summarized in Fig.1.

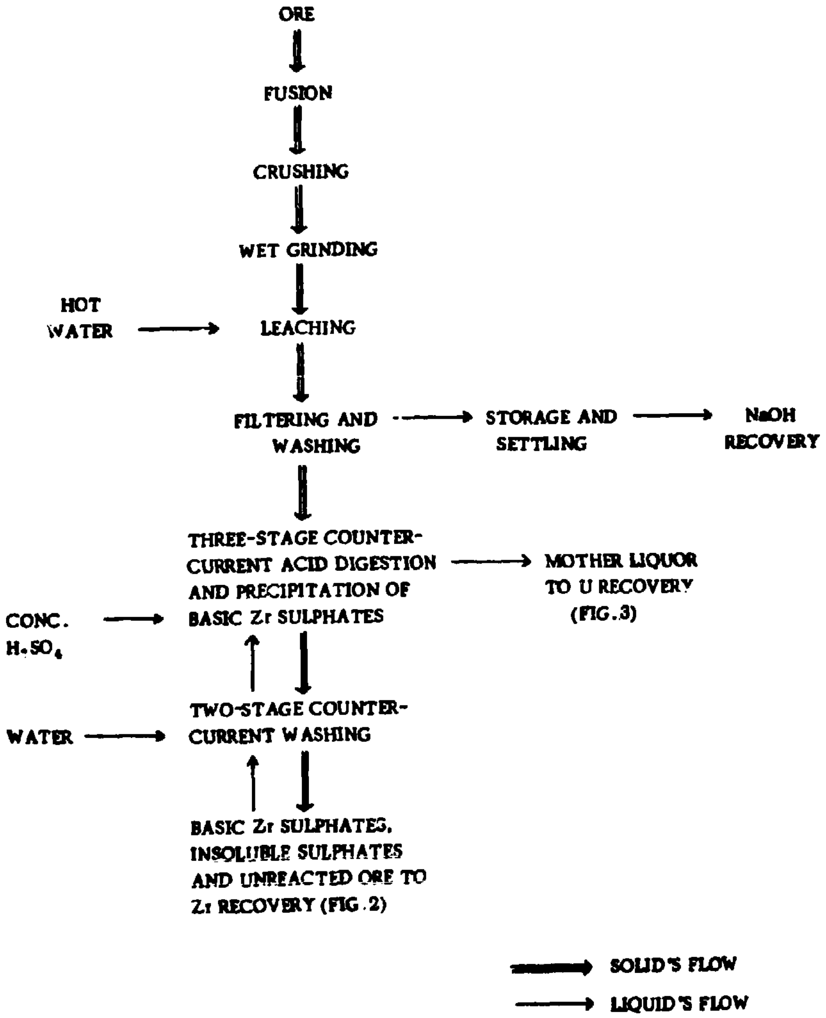

Fig. 1. Alkaline fusion and uranium - zirconium separation.

The alkaline mass from the fusion step is crushed, wet ground and leached with hot water (60°C) for 1 hour with a liquid/solid ratio of l/l, in order to eliminate the excess soda, sodium silicate and other soluble products. The resulting pulp is washed for removal of traces of NaOH which would raise unnecessarily the acid consumption in the subsequent acid treatment. The pulp contains most of the zirconium as a sodium zirconate, Na_2ZrO_3, there probably being also some sodium zirconium silicate, $Na_2Zr(SiO_4)_2$. Uranium occurs in the form of sodium uranate.

The washed pulp is now subjected to a sulphuric acid treatment in a three-stage countercurrent contactor-decanter battery at the temperatures of 40, 60 and 90°C, respectively, along the pulp path. The sodium zirconate is dissolved at the higher temperature in

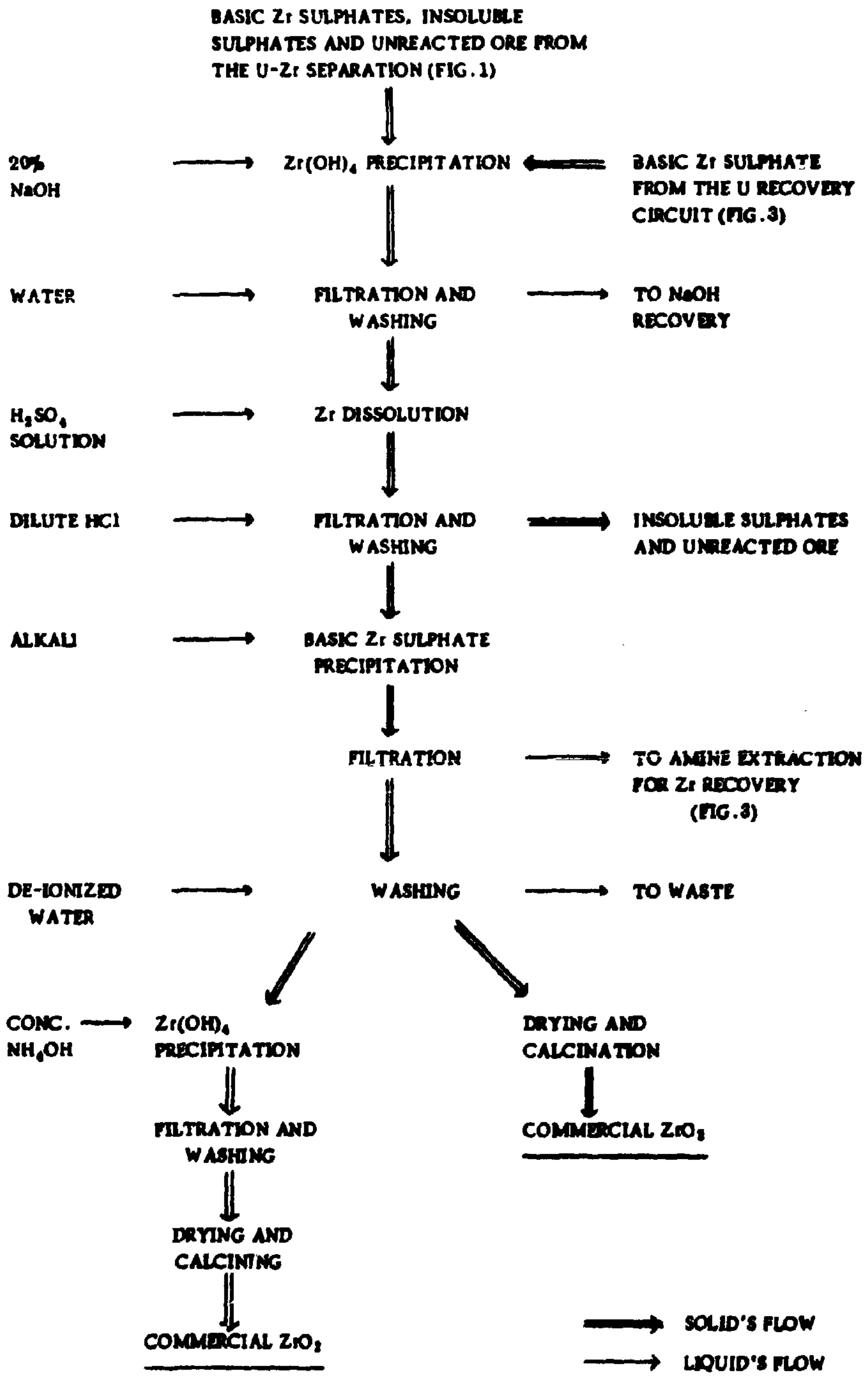

Fig. 2. Iron-zirconium separation and ZrO_2 production.

contact with the strong incoming acid, forming a soluble zirconium sulphate, which precipitates as a basic sulphate at the lower temperatures, when the zirconium sulphate solution contacts the incoming alkaline pulp of the first stage.

Conditions are so adjusted that the outgoing sulphuric liquor to the uranium recovery circuit (Fig.3) is approximately 0.3N H_2SO_4. An analysis of the main constituents of this stream yielded approximately 0.75 g/litre U_3O_8, 15 g/litre ZrO_2 and 260 g/litre SO_4^{2-}. Acid consumption at this stage amounts to 1.4 ton H_2SO_4/ton ore. The resulting solids containing the basic zirconium sulphates, other insoluble sulphates and the unreacted ore are washed with water and sent to the ZrO_2 production circuit (Fig. 2).

Iron - zirconium separation and ZrO_2 production

The recovery of the zirconium in the ZrO_2 production circuit is done by dissolving the basic zirconium sulphates. This is first carried out by repulping the solids with a hot 20% NaOH solution. A thick slurry of the sulphates is added to the hydroxide in order to maintain an excess of soda at all times. This procedure prevents the formation of a fine suspension of the rather refractory $ZrO(OH)_2$, preferentially forming the hydroxide $Zr(OH)_4$. A slurry containing the zirconium hydroxide is now added to a hot sulphuric acid solution, which re-dissolves the zirconium as the soluble sulphate. Filtering this solution separates the zirconium from the insoluble sulphates and the unreacted ore.

The iron - zirconium separation and decontamination from titanium, aluminium and other impurities is done by a newer precipitation of basic zirconium sulphates. This precipitation can be carried out according to conditions prescribed by different workers [6 - 8], yielding up to 99% zirconium recoveries when a basic sulphate of the formula $Zr_5O_8(SO_4)_2 \cdot x H_2O$ is precipitated [9]. The precipitation can be effected by any of the existing procedures, but when solutions are too concentrated the recovery is only partial and more than one precipitation stage is required. The method employed in this work consisted of the adjustment of the pH value of the solution to 1.7, followed by heating to 90°C. Two precipitations under these conditions can reduce a 50 g/litre ZrO_2 solution to 5 g/litre ZrO_2. The partial precipitation of sulphates yields a better decontamination from iron, especially in the presence of a small amount of HCl. The 5 g/litre ZrO_2 filtrate can be sent to the uranium recovery circuit for a joint recovery extraction.

The basic sulphate after successive water washings is sufficiently free from iron, titanium and aluminium to warrant a direct drying and calcination to yield a commercial grade of zirconium oxide with less than 0.09% Fe. The sulphate can also be further treated with ammonia to give the $Zr(OH)_4$ which is washed, dried and calcined to the oxide. Lower sodium and sulphur contents in the final product are obtained in this case.

Recovery of the uranium values

The recovery of uranium (Fig.3) is done by solvent extraction of the sulphuric liquor leaving the countercurrent contactor - decanter battery (Fig.1). The liquor is firstly adjusted to a pH value of I.7 with a lime slurry which lowers somewhat its sulphate contents. The hydrated calcium sulphate precipitate is filtered and washed with water. Uranium losses in this operation are negligible. The filtrate and washings are now combined and heated to precipitate part of the remaining zirconium as a basic sulphate. This precipitated sulphate is sent to the ZrO_2 production circuit. After this conditioning treatment, the solution is ready to enter the uranium extraction circuit. The composition of the liquor at this stage is aproximately 0.55 g/litre U_3O_8 and 2.0 g/litre ZrO_2. The Zr/U ratio in this feed liquor must not exceed 10/1, otherwise the uranium extraction will be greatly reduced. The still high concentration of sulphates (~ 200 g/litre SO_4^{2-}) affects adversely the uranium distribution coefficient. However, this effect is smaller than the one caused by a high Zr/U ratio.

In the extraction of uranium and of the remaining zirconium, an organic phase consisting of 7.5 Varsol % Alamine 336[1] in an inert diluent, Varsol[2], is employed. Contacting is carried out at 30°C with an org./aq. ratio of 0.3 in four equilibrium stages. Uranium extraction is nearly complete under these conditions and more than 85% of the zirconium is extracted. No objectionable side effects, such as emulsion or second organic phase formation, occur at this stage. A certain amount of iron (Fe^{3+}) is extracted along with the U and Zr, but it can be eliminated by a two - stage water scrub. Joint re - extraction of U and Zr is performed by a 30 g/litre Na_2CO_3 solution, at 30°C, in two equilibrium stages. Uranium and zirconium are completely re - extracted, but soon after the solution goes cloudy, a process that is accelerated by heating, and ends up with the precipitation of a white, flocculent, easily, filtered precipitate of carbonated zirconia, $(Zr_2O_3(OH))_2\ CO_2 \cdot 7\ H_2O$, carbonated tri - oxo - di - zirconium hydroxide heptahydrate [9]. When the initial aqueous phase is heavily loaded with zirconium, the re - extraction cannot be done by an alkaline carbonate, because the carbonated zirconia precipitates in a gel - like form in the organic phase. The carbonated zirconia can be marketed directly after drying, or calcined to yield a high - grade zirconium oxide. Approximately 6% of the original zirconium ends up as the carbonated zirconia.

The filtrate and combined washings of the carbonated zirconia precipitation contain the uranium as the uranyl tricarbonate complex. Addition of an alkaline hydroxide to the warm solution precipitates the corresponding uranate.

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[1] A mixture of tertiary amines, consisting mainly of tri - n - octylamine and tri - n -decylamine, manufactured by General Mills, Inc., USA.

[2] A paraffinic naphtha fraction, containing approximately 18% of aromatic hydrocarbons, manufactured by Esso Standard do Brasil, Brazil.

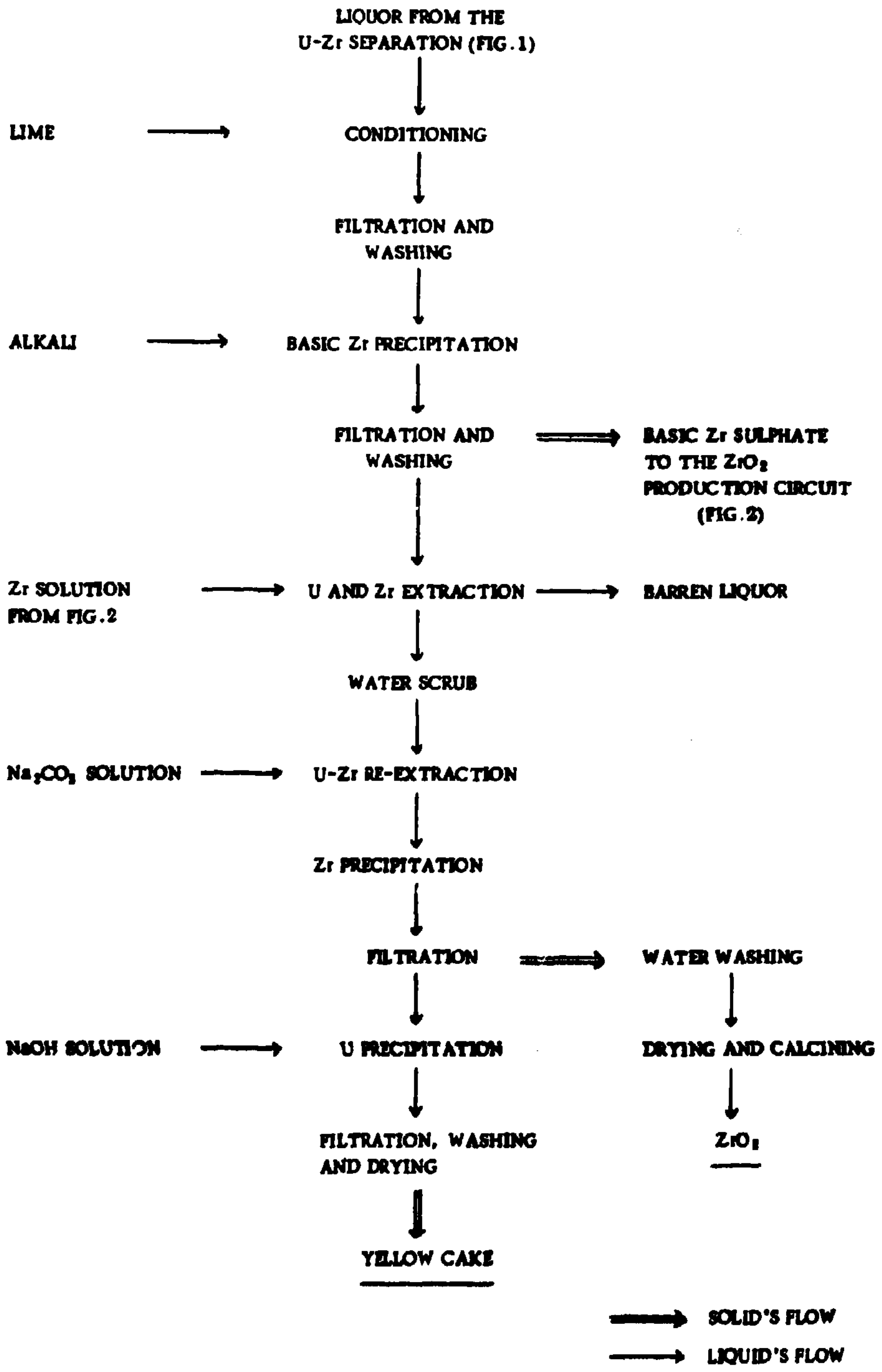

Fig. 3. Uranium recovery.

ECONOMIC EVALUATION

A preliminary economic analysis of the proposed flowsheet was carried out in order to evaluate the order of magnitude of production costs of ZrO_2, by charging the whole of the uranium processing expenses to the ZrO_2. As expected, NaOH consumption was the most significant cost element, representing over 40% of the raw materials costs. Estimated production costs for the ZrO_2 were calculated to range from Cr\$5,50 (new cruzeiros) to Cr\$6,00 per kg ZrO_2. The lower figure is obtained when credit for the 24.5% excess NaOH is allowed for. The Brazilian import market in the year 1969 amounted to about 165 tons of commercial grade ZrO_2 at a cost of Cr\$9,00 CIF[3] Santos, Brazil, in the latter part of that year.

CONCLUSIONS

The investigated processing scheme, consisting of well - established intermediate processes may be a satisfactory solution to the age - long problem of the recovery of the uranium and zirconium values from the caldasite. However, the ore cannot be considered as a primary uranium source, in view of its nature, which entails marketing approximately 200 parts of ZrO_2 for every part of U_3O_8 produced. On the other hand, processing for the ZrO_2 content per se is highly attractive on account of the rather large reserves of the high - grade ore.

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[3] CIF = Cost Insurance Freight.

DISCUSSION

A. FAURE (Chairman): In the optimization of the extraction of zirconium by the method of steepest ascent, what specifically is the response variable that is being optimized?

A.E.P. BROWN: It is the solubilization of zirconium content in the caldasite. Around the optimum point as determined by this method, it is possible to achieve 97% zirconium solubilization and 100% uranium recovery.

E. CALMON COSTA: As co - author of the paper I should like to add that the response variable employed in the fusion study was rather the ZrO_2 extraction. At the optimum point indicated by Mr. Brown, extraction of ZrO_2 is indeed higher than 97%. Around the optimization point there is a plateau on the extraction versus NaOH/ore ratio curve which begins at approximately 1.7 g NaOH/g ore, and therefore this ratio corresponds to the minimum ratio required for 97% ZrO_2 extraction. The uranium is entirely extracted by fusion and the subsequent acid digestion.

RESUMO

Investigou-se um esquema para o processamento químico do caldasito, uma mistura de zircão e de baddeleyita, abundante na região de Poços de Caldas, visando uma recuperação conjunta do zircônio e do urânio a partir do minério. As separações urânio - zircônio e ferro - zircônio foram realizadas pela precipitação de sulfatos básicos de zircônio. O urânio foi recuperado por extração da água mãe da primeira precipitação do zircônio, empregando-se Alamina 336 em um diluente inerte. Os produtos finais foram o diuranato de sódio e o óxido comercial de zircônio. Os custos estimados de produção comparam-se favoràvelmente com os preços da importação brasileira.

RÉSUMÉ

On a étudié un schéma du procédé pour obtenir une double récupération d'uranium et du zirconium contenus dans la caldasite, une mixture de zircone et de baddeleyite, dont le plateau de Poços de Caldas a des grandes ressources. La séparation des couples uranium - zirconium et fer - zirconium a été faite par l'extraction des eaux - mères de la première précitation du zirconium en employant l'alamine 336 avec un diluant inerte. Les produits finals sont le diuranate de sodium et l'oxide commercial de zirconium. Les coûts estimés de production sont favorablement comparés avec les prix d'importation brésiliènne.