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Production of thorium nitrate from
uranothorianite ores

par

M. BRODSKY

Société Potasse et Engrais chimique

et

R. SARTORIUS and Y. SOUSSELIER

Commissariat à l'Énergie Atomique

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BRODSKY M., SARTORIUS R., SOUSSELIER Y.

Rapport CEA n° 1 118

Production de nitrate de thorium à partir de minerais d'uranothorianite.

Sommaire. — On discute de la séparation du thorium et de l'uranium de minerais d'uranothorianite, soit par précipitation, soit par extraction, soit par solvants et on décrit un procédé industriel pour la fabrication du nitrate de thorium.

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PRODUCTION OF THORIUM NITRATE FROM URANOTHORIANITE ORES

By M. BRODSKY*, R. SARTORIUS† and Y. SOUSSELIER†

Abstract—The separation of thorium and uranium from uranothorianite ores, either by precipitation or solvent-extraction methods, are discussed, and an industrial process for the manufacture of thorium nitrate is described.

URANOTHORIANITE ores, sometimes incorrectly called thorianite, are mixed thorium and uranium ores in which these two elements are present in the form of the tetravalent oxides, thorium oxide and uranium oxide. These ores should not be confused with uranothorite ores, which are composed of uranium and thorium silicates.

Uranothorianite ores are comparatively rare. The richest deposit known at present is in Madagascar: in the South-East part of the island near Fort-Dauphin. Other deposits notably in Siberia, are mentioned in the literature. The Madagascar deposits are generally found in the form of placers, in which the uranothorianite is concentrated. The accumulation is thought to be due to the erosion of pegmatites.

The uranothorianite is composed of very dense cubic crystals (density 8), in which the oxides of thorium and uranium are co-crystallized in various proportions. The ratio of thorium to uranium is between 8 and 3. Owing to the high density of uranothorianite, gravimetric pre-concentration methods can be used at the mine when the uranium plus thorium content of the ore is considered insufficient.

Besides its two fundamental components, the Madagascar uranothorianite contains lead (1–3%), iron (1–2%), rare earths (sometimes more than 1% of cerium) and titanium and tin in lesser quantities; there are no alkalis present. The gangue is siliceous and its proportion, which depends on the pre-concentration, can be less than 1%.

As an example, the results of analyses of three samples from Madagascar are as shown on p. 69.

EXTRACTION AND SEPARATION OF THORIUM AND URANIUM

The chemical treatment aims at separating the uranium and thorium from the other elements present, and then from each other. In particular, iron and rare earths are undesirable because of their neutron-absorption properties. The thorium should be freed from uranium, which otherwise would dilute the uranium-233 formed by irradiation; conversely the presence of thorium in

* Société Potasse et Engrais Chimiques, Villeneuve-la-Garenne, Seine, France.

† Commissariat à l'Énergie Atomique, Fontenay-aux-Roses, Seine, France.

	Composition (% w/w)		
UO ₂	17.06	22.18	23.90
ThO ₂	77.20	72.15	60.40
CeO ₂	1.00	1.25	1.56
PbO	1.91	1.40	1.17
Fe ₂ O ₃	1.45	1.70	2.15
TiO ₂	0.15	0.14	1.07
SnO ₂	0.28	0.20	0.18
Al ₂ O ₃	—	—	1.13
SiO ₂	0.40	0.48	2.30
CaO	—	—	0.92
MgO	—	—	0.84
BaO	—	—	0.29

uranium reduces the reactivity of the latter in the reactor and complicates the recovery of plutonium.

In practice, the separated uranium should not contain more than 100 g of thorium per ton, and thorium of nuclear purity should not contain more than 1 g of uranium or more than some tens of grammes of iron and lead per ton.

Because such a high purity is rather difficult to attain directly, it was decided to try to produce only a thorium containing some tens of parts per million of other elements (uranium, iron, rare earths etc.)

The treatment of uranothorianite ore consists in dissolving the ore in nitric acid and then separating thorium from uranium and impurities (cerium, lead, iron). Different processes can be considered, based either on chemical separations or on extractions by selective solvents. Figure 1 shows the main routes possible. It is obvious that many other schemes could be put forward.

First we shall examine the chemical separations and then the solvent extractions.

Chemical Separations

Separation by precipitation of thorium sulphate—Sodium sulphate, followed by sodium carbonate until the required pH is reached, are added to the diluted solution. The precipitated thorium sulphate is removed by filtration; the uranium remains in solution.

This process involves cheap reagents, and when precipitated under well-defined conditions, the thorium sulphate is easy to filter. However, appreciable quantities of uranium, which become greater as the basicity is increased, are co-precipitated. When the precipitation is stopped at a high acidity, the greater purity of the precipitate is offset by a decrease in the insolubility of the thorium.

The most favourable precipitation conditions correspond to a maximum concentration of 80 g/l. of thorium oxide, a temperature of 60°C and 1.2 kg of sodium sulphate per kilogram of thorium oxide. Under these conditions, if sodium carbonate is added until the pH is 3.5, all the thorium is rendered insoluble, but the precipitate retains more than 0.1% of uranium. If the neutralization is stopped at pH 2, the precipitate contains no more than 0.02% of uranium but more than 5% of the thorium remains in solution.

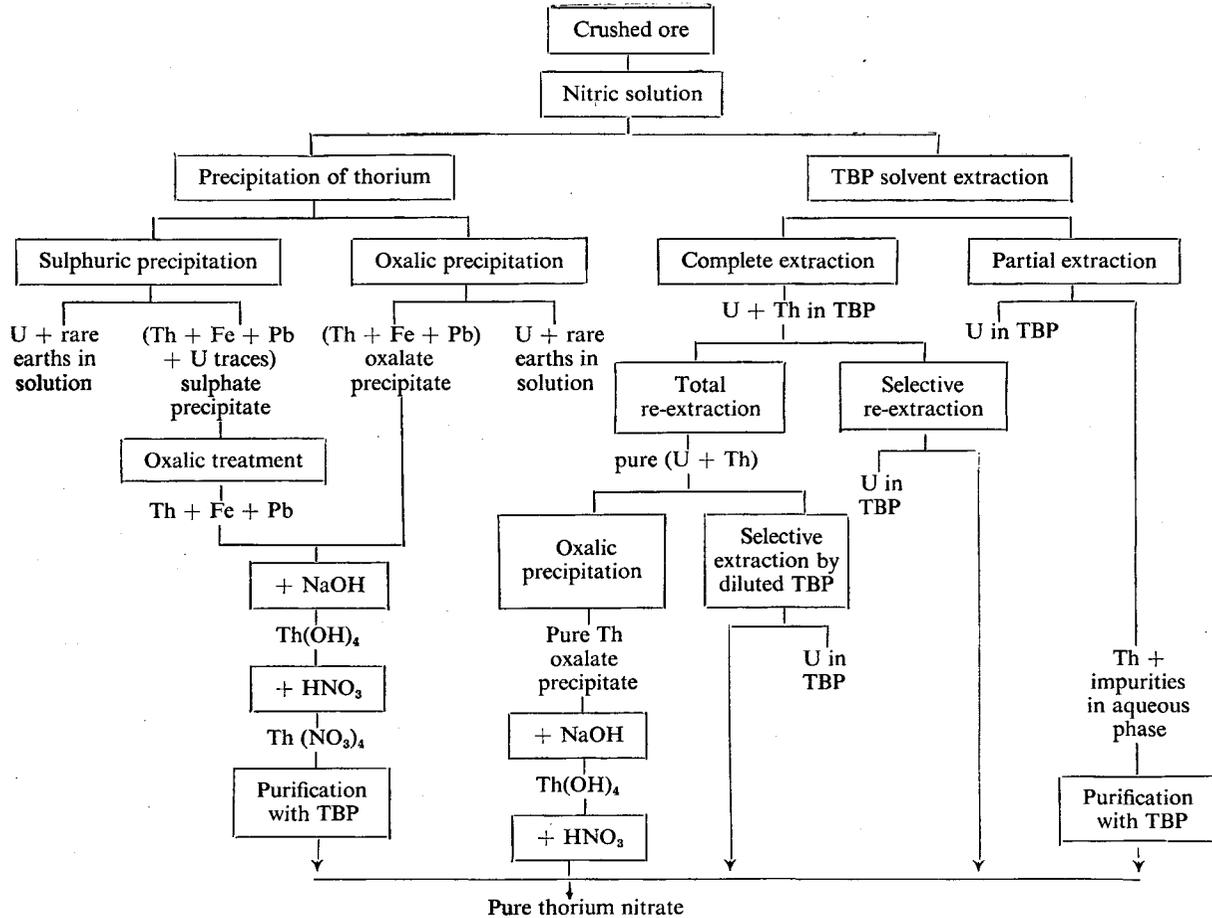


Fig. 1. Outline of different processes.

The retention of uranium by the precipitate increases rapidly with the thorium concentration of the initial solution but does not appear to be influenced by the temperature. Retention of cerium, on the other hand, increases with temperature. The cerium content of the precipitate rises from 0.05 to 0.1% as the temperature rises from 20 to 90°C. Lead is precipitated with the thorium and most of the iron is also found in the precipitate.

The thorium-uranium separation can be considerably improved by a double precipitation. Hence, if the thorium sulphate obtained as described above, is partly redissolved in 0.5 N nitric or sulphuric acid and reprecipitated by adding some oxalic acid, the yield of thorium is 97% and the uranium present amounts to only 30 g per ton.

Separation by precipitation of thorium oxalate—Crystallized oxalic acid is added (1 kg of oxalic acid dihydrate per kilogram of thorium oxide) and, after one hour of mixing at 90°C, the thorium oxalate is filtered off and washed. The thorium yield increases with the quantity of oxalic acid used, but the higher the yield, the greater is the retention of uranium, cerium and lead. The separation of cerium is improved by an increase in temperature.

Precipitation of the oxalate gives a more efficient separation of thorium from uranium than does precipitation of the sulphate. Thorium oxalate, precipitated with a 99% yield contains only 0.02% of uranium. Under the same conditions, however, the thorium oxalate carries about 10% of the lead, 5% of the iron and nearly all the cerium.

An almost perfect separation of thorium from uranium can be achieved by dissolving the thorium oxalate in ammonium carbonate solution and treating the resulting solution with hot concentrated nitric acid. With pH 1.2 at the end of the operation, the re-precipitated thorium oxalate contains only 1 p.p.m. of uranium although it is still contaminated by rare earths.

Double precipitation of thorium—The two methods of separation described above give sufficiently pure thorium salts only at the expense of an incomplete precipitation of thorium. A higher yield can be obtained by precipitating the thorium in two steps. In the first, most of the thorium is thrown out of solution by one of the two above methods: at a high acidity in the case of the sulphate precipitation, or with an oxalic acid deficiency in the second method. In either case the filtrate still contains about 1 g of thorium oxide per litre. This thorium is precipitated in the second step by the addition of oxalate or fluoride ions.

If oxalic acid is used, a higher pH must be maintained and an excess of oxalic acid. The best conditions are as follows: temperature, 80°C; final acidity, pH 2; quantity of oxalic acid, 1 part to 1 part of thorium oxide plus 5 g excess of acid per litre of solution. The whole of the thorium is then precipitated together with the lead and a little of the uranium. This second precipitate must be recycled to the first step.

In the separation by fluoride precipitation sodium fluoride is added at pH 2. The thorium is quantitatively precipitated, carrying all of the cerium but none of the uranium.

Separation by precipitation of thorium pyrophosphate—Thorium is separated by pyrophosphates in the treatment of monazites with a high rare-earth content. Since pyrophosphates in excess do not precipitate uranyl salts, their use seemed

promising in the treatment of uranothorianite. Experience has shown however that the precipitate carries a large amount of the uranium: up to 8%, if the thorium precipitation is complete, and about 2% if the thorium yield is only 93%.

Solvent Extraction

Thorium and uranyl nitrates are soluble in certain oxygenated organic solvents such as tributyl phosphate (TBP). This property is currently used in the uranium industry and can be applied in the treatment of uranothorianite.

By this method thorium and uranium nitrates may be extracted simultaneously (GRESKY, 1956) leaving the other metals except part of the cerium in the aqueous phase. It also provides a method for separating thorium from uranium and for the further purification of thorium.

Simultaneous extraction of thorium and uranium nitrates—Uranyl nitrate is extracted more readily than thorium nitrate. Simultaneous extraction of these two salts is possible, in the presence of a salting-out agent (Table 1).

Table 1. Equilibria in Uranyl Nitrate-TBP and Thorium Nitrate-TBP Systems

Initial solutions		(Solvent: 40% TBP in dibutyl ether acidified to 0.5 M HNO ₃ . Aqueous: 2 M HNO ₃ with uranyl or thorium nitrate. Vol. Organic/Vol. Aqueous = 1)			
		Uranium		Thorium*	
Aq. (g/l.)	Org. (g/l.)	Aq. (g/l.)	Org. (g/l.)		
115	150	200	87		
70†	140†	130	70		
35	120	80	55		
16	97	60	40		
1	15	20	12		

* See also MCKAY and FLETCHER (1956) for comparable data under modified conditions.

† Interpolated value.

Ammonium, calcium and sodium nitrates are possible salting-out agents for thorium (GRESKY, 1956). Since the presence of calcium in the raffinate from the column interferes with the subsequent decontamination treatment, the best agent to use is sodium nitrate, being cheaper than ammonium nitrate. It can be made conveniently by partly neutralizing the acidity of the solution derived from the ore. The nitrates of iron and lead are also good salting-out agents and facilitate the extraction of thorium when the solution contains sulphates or phosphates (Table 2).

Cerium nitrate, as found at this stage of the process, is not readily extracted by TBP and nearly all of the cerium which is extracted by the solvent can be removed

Table 2. *Extraction of Thorium. Repression by Oxalate, Sulphate and Phosphate Ions in the Absence and Presence of Ferric and Lead Nitrates*

Solvent: 33% TBP in kerosene appropriately acidified with HNO_3
Vol. Organic/Vol. Aqueous = 1.

Initial aqueous phase						Thorium at equilibrium*	
HNO_3 (M)	Oxalate (g/l.)	Sulphate (g/l.)	Phosphate (g/l.)	$\text{Fe}(\text{NO}_3)_3$ (g/l.)	$\text{Pb}(\text{NO}_3)_2$ (g/l.)	Aq. (g/l.)	Org. (g/l.)
0.5	—	—	—	—	—	10	27
0.5	1	—	—	—	—	10	20
0.5	1	6.5	—	—	—	10	10
1	1	6.75	—	3.5	10.6	10	24
0.5	1	—	1	—	—	10	16
1	1	6.75	1	3.9	10.6	10	20

* Expressed as ThO_2 .

by washing with a solution which is N in nitric acid and 2 N in sodium nitrate. In this way, from an ore containing 1% of cerium, thorium nitrate containing less than 50 p.p.m. of cerium may be obtained. The organic extract can be stripped of thorium and uranium with water.

Diluted TBP is used. The diluents used in the manufacture of uranium (paraffin hydrocarbons corresponding to a kerosene fraction) sometimes give rise to the appearance of a third phase with solutions of thorium nitrate (McKAY and FLETCHER, 1956). These phenomena may be avoided either by choosing non-paraffinic diluents, e.g. dibutyl ether, or by regulating the respective concentrations of thorium and salting-out agents.

Uranium-thorium separation—A method of separating uranium nitrate from thorium nitrate can be based on the difference in their behaviour towards the solvent TBP (WELLS and NICHOLLS, 1956; GRESKY, 1956).

Two methods have been proposed. In the first, uranium only is extracted initially, and the thorium remaining in the aqueous raffinate is passed to a further column for purification. In the second method, which is probably the easier in practice, there is simultaneous extraction of uranium and thorium which are then separated from one another by separate selective strips (c.f. GRESKY, 1956).

AN INDUSTRIAL PROCESS FOR THE MANUFACTURE OF THORIUM NITRATE

The process described below gives crystallized thorium nitrate from Madagascar ore. It consists essentially in dissolving the ore in nitric acid, purification by solvent extraction and thorium-uranium separation by thorium oxalate precipitation (Fig. 2).

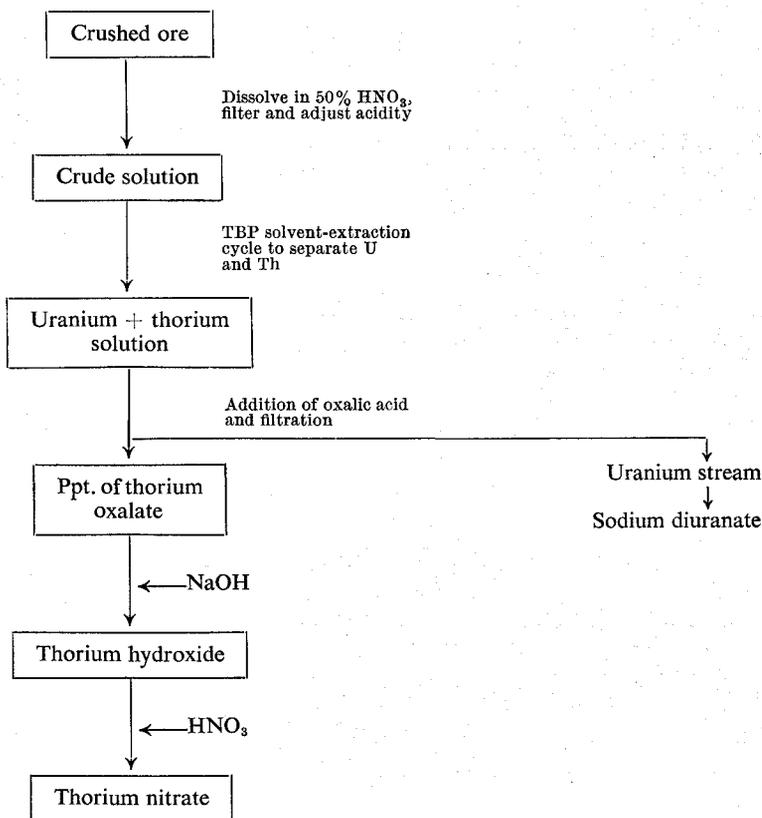


Fig. 2. Outline of industrial process for preparation of thorium nitrate.

Preparation and Solution of the Ore

The ore, after being crushed to pass a 12 mm sieve, contains up to 10% by weight of water. In order to dissolve as much of the thorium as possible, grinding to a fine size and a high acid concentration are necessary. The ore is therefore dried, ground to —120 mesh in a ball-mill and treated with boiling 50% nitric acid for 8 hr, the insoluble residue being separated on a rotary drum filter coated with silica. The proportion of insoluble matter varies from one batch of ore to another; when the ore contains 85% of thorium and uranium oxides the insoluble matter usually represents some few per cent of the weight of the ore. The thorium and uranium are almost completely dissolved, the loss being of the order of 0.1% of uranium and 0.5% of thorium. Since very efficient washing is desirable, two successive filtrations with intermediate repulping are performed in cases where the proportion of residue is high.

Solvent Extraction

The aqueous product, which is about 5 N in acid, is neutralized with solid sodium carbonate to a final acidity between 1.5 and 1.8 N. It then contains

about 250 g of thorium oxide per litre, and a quantity of uranium which varies according to the origin of the ore.

The extraction is done with TBP, diluted to 33% with kerosene, in mechanically agitated columns of a type similar to the Rotating Disk contactor. Two columns, in each of which the height agitated is 2 m, are linked in series. The extract is washed with a solution N in nitric acid and 2 N in sodium nitrate. The solvent to aqueous ratio is 4, and the solvent to scrub ratio is 10.

The raffinate contains less than 0.3 g of thorium oxide per litre and only traces of uranium. The washed extract, which contains practically no cerium, iron or lead, is treated with acidified demineralized water in a single column, identical with the extraction columns. The aqueous re-extraction and solvent-extraction rates are the same. The regenerated solvent contains from 1 to 3 g of uranium per litre, and only traces of thorium.

Precipitation of Thorium Oxalate

The aqueous solution from the previous cycle contains practically no metals other than thorium and uranium, the concentration of the former being to 40 g/l. of thorium oxide. It is treated at 90°C with one part of oxalic acid dihydrate to one part of thorium oxide in an agitated vessel as a batch operation.

The thorium oxalate suspension is filtered on a horizontal rotating filter composed of separate segments. After being washed twice, the thorium oxalate cake contains 200–500 parts of uranium per million. Filtration is done with Dacron cloth, and since the precipitate is very fine, the filtrate must be clarified before precipitation of the uranium. In the clarified filtrate the thorium to uranium ratio is of the order of 1 : 1000.

Precipitation of Sodium Uranate

The uranium in the clarified filtrates is precipitated by sodium hydroxide. The sodium uranate, separated by an automatic filter press, is used for the manufacture of uranium metal.

Conversion of the Thorium Oxalate to Thorium Hydroxide

The thorium oxalate cake is dispersed in demineralized water so that the final concentration is the equivalent of 40 g of thorium oxide per litre of suspension. The thorium is converted to hydroxide by the addition of one part of sodium hydroxide to one part of thorium oxide; the caustic soda is added to the cold suspension, then the whole is brought to 90°C and agitated for 6 hrs. The thorium hydroxide is separated on a rotary drum filter lined with nylon cloth. The conversion is practically quantitative.

Solution of the Thorium Hydroxide and Crystallization of the Nitrate

The thorium hydroxide is dissolved in concentrated nitric acid. The thorium nitrate solution (350 g of thorium oxide per litre) is concentrated and crystallized in a continuous system of the Oslo Krystal type.

The thorium nitrate crystals, separated on a continuous centrifuge dryer, contain approximately 50 parts of uranium per million of thorium, and half as much iron and silica. Only traces of chloride, sulphate and phosphate are present.

Treatment of Radioactive Effluents

In view of the high thorium and uranium content of the ore, an industrial plant for the treatment of uranothorianite must include safety devices to protect the staff against the dangers of radioactivity. Treatment with acid, precipitation and filtration must be done in well-sealed apparatus, linked to an adequate ventilation system. Manipulation of the ore and its physical preparation must be remotely controlled and require efficient devices for removing dust.

It is essential to treat the raffinate (from the solvent-extraction column) before disposal, since it contains all the radium and radio-lead. A satisfactory decontamination is obtained by precipitating lead sulphate together with the radium sulphate, at pH 6 (see page 104). The decontamination factor obtained in a single operation is better than 1000, and can reach 10,000. It is necessary to add lead as a carrier if the ore does not contain sufficient.

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