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Refining of uranium concentrate and production of uranium oxide and metal

by

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The paper presents the processes used in Sweden for the production of uranium oxide and metal from uranous phosphate concentrate.

The refining process involves digestion of the uranous phosphate with caustic soda, conversion of the uranous hydroxide to ammonium uranyl carbonate, dissolution in nitric acid, and purification by solvent extraction using hexone. Ammonium uranate is recovered from the pure uranyl nitrate solution by homogeneous precipitation with urea. After calcination the UO_3-product is reduced to UO_2, converted to UF_4 in a "dryway" hydrofluorination process and reduced by calcium to U-metal, which subsequently is remelted under vacuum.

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Refining of Uranium Concentrate and Production of Uranium Oxide and Metal

by

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This paper presents the processes used at AB Atomenergi, Stockholm, for the production of uranium oxide and metal from uranous phosphate concentrate. A previous Geneva Conference paper (1) described the production method for the uranium concentrate.

The simplified flow-sheet in figure 1 shows the chemical processes which are used for converting the uranous phosphate concentrate to uranium trioxide of high purity. The two steps which are called caustic digestion and carbonate process, were developed in 1949-51 at the Dept. of Industrial Inorg. Chemistry of the Royal Institute of Technology, Stockholm, by professor O. Stelling and his coworkers.

The production of UO_2 in a suitable form for sintering as well as the production of U metal ingots, follows the now more or less classic processes. The reduction and fluorination techniques were developed at the Company. The adopted technique for the fluoride reduction to U metal is, however, essentially a modification of the French procedure.

Refining of Uranium Concentrate

Caustic digestion

The most important components of the uranium concentrate are given in table 1. Uranium occurs as uranous phosphate. The purpose of the caustic digestion is to remove the phosphate by converting uranous phosphate to uranous hydroxide and soluble sodium phosphate according to the reaction

$$U(HPO_4)_2 + 6NaOH = U(OH)_4 + 2Na_3PO_4 + 2H_2O$$

The digestion is done with 2N sodium hydroxide solution at 95°C in two stages. The amount of caustic soda is 2.5 kg/kg of U and the retention time 2 hours in each stage.

As most of the phosphate is dissolved in stage I and only a small part of it in stage II the consumption of sodium hydroxide in stage II is very small. The solution which has been separated from the uranous hydroxide in stage II can therefore go to stage I after a small adjustment of its sodium hydroxide concentration.

The uranous hydroxide is very difficult to filter so the sodium phosphate solution is separated from the uranous hydroxide by sedimentation and decantation. After stage II the sludge of uranous hydroxide is washed with water in two stages.

Table 2 gives an analysis of the most important components of a dried sample from the alkali digested product. Comparison with the analysis of the uranium concentrate (table 1) shows that the caustic digestion has greatly reduced the concentration of both phosphate and aluminium.

Carbonate Process

The uranous hydroxide slurry from the caustic digestion is oxidized with hydrogen peroxide and treated with ammonium bicarbonate at 60-70°C for 1 hour. Most of the uranium is dissolved but the impurities to a great extent remain in the insoluble residue. The residue is very difficult to filter. Diatomaceous earth is used as an aid to filtering.

A small amount of sodium fluoride is added in the process. By this fluoride additon it is possible to reduce the concentration of rare earths in the solution very effectively.

The filtrate including wash solution flows to a crystallizer. Ammonium uranyl carbonate, $(NH_4)_4UO_2(CO_3)_3$, is crystallized by addition of ammoniumbicarbonate and by cooling the solution to about 10°C. Before the crystallization the uranium concentration of the solution is about 50 g/l and after crystallization 1.5 - 3.0 g of U/l. The crystalline product is filtered and washed with saturated ammoniumbicarbonate solution. About 50% of the filtrate is recirculated in the process and the rest is treated in the following way. The pH of the solution is reduced to 5 by additon of sulphuric acid and the solution brought to boiling. Carbon dioxide is boiled off and uranium precipitated as uranate which is filtered and recirculated to the dissolution in ammonium bicarbonate solution.

The insoluble residue from the carbonate process contains too much uranium for discharge so it is brought back to the shale leaching step. An analysis of a sample from ammoniumuranylcarbonate is given in table 3. The concentration of impurities with high neutron absorption is low.

Solvent extraction

Ammonium uranyl carbonate from the carbonate process is dissolved in nitric acid and calcium nitrate added to get a solution containing, per litre, about 200 g of uranium, 0.7 M free HNO_3 and 3 M $Ca(NO_3)_2$. The solution is extracted in a multistage mixer column with hexone (methyl isobutyl ketone). Flow ratio organic phase: aqueous phase is about 1. The uranium in the organic phase is stripped with distilled water. Flow ratio organic phase: aqueous phase is about 1. The columns are 6 in. diam. glass tubes (Pyrex) with plates, baffles and impellers of stainless steel. The streams are fed to the columns from stainless steel pressure vessels and the flow rate measured with rotametres.

Homogeneous Precipitation

The uranium in the nitrate solution from the solvent extraction has sufficiently high purity. The problem is to convert it to a form suitable for the dry-way processes. Precipitation from homogeneous solution is used.

The fundamental reaction of the process is the hydrolysis of carbamide at elevated temperature:

$$(NH_2)_2CO + H_2O = 2NH_3 + CO_2$$

The carbon dioxide disappears from the acid uranyl nitrate solution, but the ammonia stays, causing a slow homogeneous increase of pH and precipitation of uranate.

The homogeneous precipitation is carried out in batches of 150 - 200 kg of uranium in a steam-jacketed reaction vessel under vigourous stirring.

The pH of the acid uranylnitrate solution from the extraction is adjusted to 2.5 - 3 and about 1 kg of urea per kg of uranium is added as a filtered solution. The solution is heated to boiling and in 2 hours the precipitation is completed. The precipitate is readily filtered.

The filtrate contains less than 10 mg of U/l. The uranate is converted to UO_3 in a tray-furnace at about 250°C. The process gives a powder which is very suitable for further processing.

Table 4 gives an analysis of the pure oxide. The concentration of impurities has been reduced to a very low level.

Table 1. Uranium Concentrate

	%
U	36.0
Al	3.9
Fe	0.8
R.E. about	0.04
PO_4	31.7

Table 2. Uranous hydroxide

	%
U	58.7
Al	0.3
Fe	1.4
R.E. about	0.04
PO_4	1.7

Table 3. UO_3 from ammonium uranyl carbonate.

Contents in ppm

B	<0.5
Cd	<1
Co	<3
Mn	<3
V	40
Ni	<3
Cr	3
Cu	9
Fe	~100
Na	<1000
Ca	~100
Ba	low
P	<30
Si	low
Sn	<3
Mg	20
Pb	<3
R.E.	not detectable

Table 4. UO_3 from homogeneous precipitation.

Contents in ppm

B	<0.5
Cd	<1
Co	<3
Mn	<3
V	<3
Ni	<3
Cr	<3
Cu	<3
Fe	15
Na	<100
Ca	<100
Ba	low
P	<30
Si	very low
Sn	<3
Mg	<3
Pb	<3
R.E.	not detectable

Production of Uranium Oxide and Metal

The procedure adopted is 1) hydrogen reduction of calcined UO_3; 2) "dry way" hydrofluorination of UO_2; 3) calcium reduction of UF_4 and 4) casting of the resulting U billets under high vacuum. Part of the UO_2 product is processed further to fluoride and metal while part of it is used as such for sintering of oxide pellets.

Although the scheme is convential in principle, some features of the adopted processes are considered quite unique and likely to be of general technical interest.

Hydrogen reduction of UO_3

The calcined UO_3 powder is reduced to UO_2 by hydrogen gas at a temperature of about 625°C or 800°C depending upon whether the oxide should subsequently be used for fluorination or sintering purposes. The reduction is carried out in a continously operating furnace (fig. 2).

The oxide powder is slowly fed through an externally heated, rotating refractory steel tube which is slightly inclined, so that the powder charge of about 10 kg will move forward under steady stirring. Hydrogen gas, in an excess of about 1.5 times the stoichiometric quantity, passes in a counter current direction over the oxide bed. The exit gas is burnt in the air and any uranium dust is subsequently vented to a wet filter system. The oxide powder is fed into the rotating tube by a screw device operating at the bottom of a stainless steel hopper which is intermittently charged with calcined UO_3 powder. At the discharge end of the furnace the UO_2 powder is continously poured out from the rotating tube into an aluminium container which can be interchanged at intervals. The capacity of the furnace unit is about 25 kg UO_2 per hour.

The homogenously precipitated UO_3 is remarkebly quick flowing and does not form any hard aggregates at the reduction temperature. The UO_2 is intentially produced in a reactive state in order to facilitate the subsequent fluorination. Hence, it has to be stored under a nonoxidizing (CO_2) gas atmosphere. The UO_2 powder has been found to be well suited for direct sintering and thus, no extra subdivision is required. The external shape of the original UO_3 "particles" are inherited. Each "particle" of UO_2 has an average size of about 40 microns and consists of a spherical aggregate composed of minute oxide crystals of an apparent size of about 1 micron or less. The sintering procedure of the UO_2 is described in details in a paper (2) also submitted to this Congress.

"Dry way" hydrofluorination of UO_2

The hydrofluorination of UO_2 is carried out at about 450°C under a flow of preheated HF gas in a continously operating furnace built according to the same general principles as the previously described reduction furnace. In this case, however, the rate of reaction is fairly slow. Yet, a production capacity of at least 10 kg per hour is obtained. Note that the two furnaces are comparable in size.

The incoming HF gas has to be preheated to about 250°C to increase the reaction rate and an excess gas quantity of about 2 times the stoichiometric requirement is needed. The exit gas, containing excess HF is neutralized in a scrubber system using a circulating 5% NaOH water solution. To maintain pressure equilibration in the furnace system some hydrogen gas is added to the HF gas.

There are some technical problems associated with this process. First of all the corrosive action of the hot HF gas on the exposed materials in the furnace has to be considered. This difficulty has been overcome by choosing pure magnesium metal as the material for the lining of the rotating steel tube as well as for the gas preheater and the screw feeding device. Any magnesium contamination of the fluoride product is not harmful. An other problem is associated with the required leak tightness of the seals between the rotating tube and the stationary end parts of the furnace. This problem has been solved in the present design by adopting the principle of a positive gas pressure seal. A positive pressure of carbon dioxide is maintained between an inner Teflon sealing ring and an outer rubber sealing ring.

Like UO_2 the UF_4 powder inherits the former shape of the original UO_3 powder particles. The bulk density is fairly low, about 1.9 g/cm^3 and the distribution range of particle sizes quite narrow. The purity of the product with respect to oxygen is remarkably low, the content of UO_2 and UO_2F_2 being each less than 0.5 %.

Our experience on the operation of these furnaces under 3 - 4 years is quite good and they appear suitable for large scale production of UO_2 and UF_4. The German company Degussa is presently making commercial units of a similar design.

Calcium reduction of UF_4

The UF_4 is reduced to U metal by calcium in a "thermite"-like batch process. Fluoride powder and 4 - 5 mm granules of calcium metal, in an excess of 10% by weight, are intimately mixed and charged in small successive portions into a cylindrical graphite container (ID 350 mm) provided with a funnel shaped transition piece to a sintered calcium cluoride crucible (ID 90 mm) at the bottom. The reaction pot is enclosed in a stainless steel container that is evacuated and refilled with argon gas to 0.8 atm before initiation of the reaction. In case the pressure during firing of the thermite mixture would rise above 1.2 atm, the spring loaded top cover of the steel vessel will open to the free air.

A normal batch operation permits the reduction of 30 kg ingots, one at a time. The yields run about 98% and a typical analysis may read as follows: C 100 ppm, Si 80, Fe 50, N 30, and B 0.15 ppm. A complete analysis is given in table 5. To minimize carbon pick up from the graphite container a thin protective layer of MgO is smeared on to its inside surface. The graphite assembly can be used repeatedly 20 - 30 times.

Table 5.

B	0.15	ppm	Na	<100	ppm
Cd	<1	"	Ca	<100	"
Co	<3	"	Al	<250	"
Mn	3	"	P	<30	"
N	30	"	Si	<80	"
V	<3	"	Sn	<3	"
Ni	6	"	Mg	5	"
Cr	<3	"	Pb	<3	"
Cu	7	"	C	100	"
Fe	40	"			

Vacuum melting and casting

The U billets are remelted under a high vacuum in an Al_2O_3-lined graphite crucible and cast into molds of graphite or steel. The tilting furnace, made by Degussa, is electrically heated by graphite resistance elements and is provided with preheating coils for the moulds. In each melting operation 400 mm long rods of 30 mm diameter are cast in groups of four, corresponding to a total weight of about 30 kg U. A melting cycle lasts about 5 hours. Castings of smaller size, about 12 mm in diameter and in groups of seven, have also been successfully produced.

Acknowledgement

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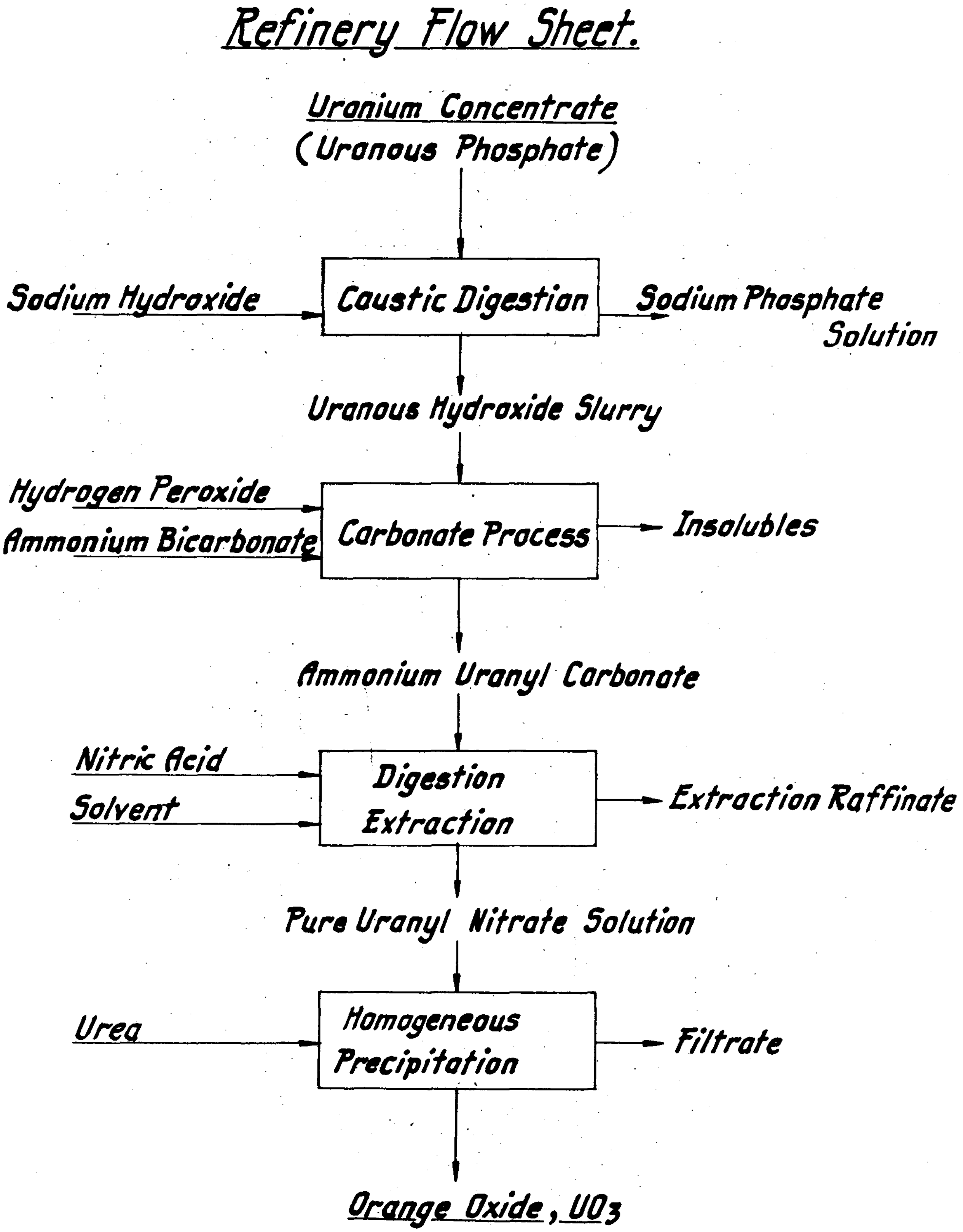

Fig. 1. Refinery Flow Sheet.

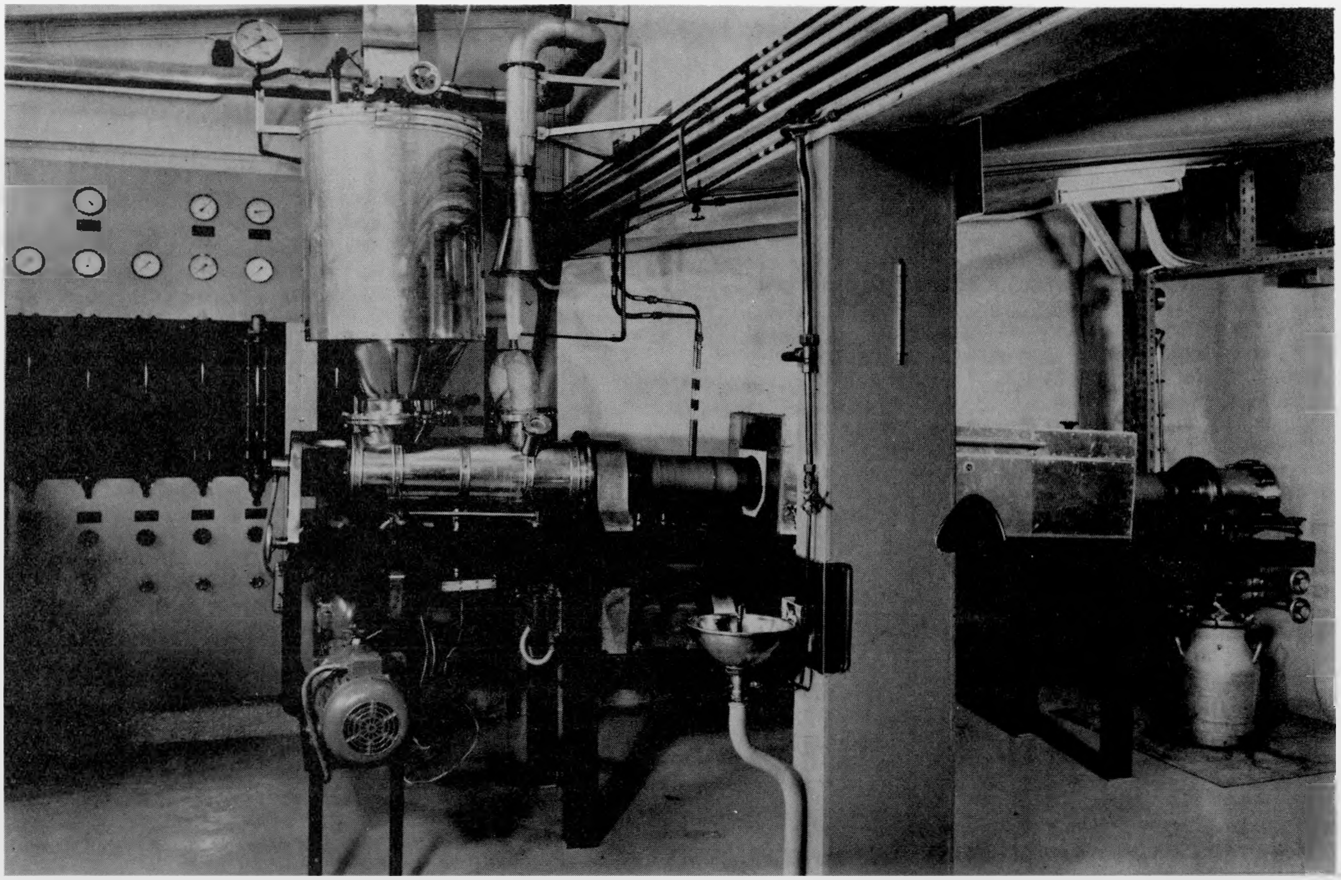

Fig. 2. Side view of the reduction furnace for UO_2 production.

At the left is seen the vertical cylindrical stainless steel hopper containing calcined UO_3 powder. A screw device transfers the powder to the furnace through the horisontal heatinsulated cylindrical part at the bottom of the hopper. The furnace with its slightly inclined refractory steel tube is shown in the middle of the picture.
To the right is the discharge end of the furnace with a UO_2 container in position. Note the burning exit gas flame close to the right side of the UO_3-hopper at the left.

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