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ABSTRACT

Recovery of U From Recycle Waste by Ion Exchange

by

I. R. Higgins

Industrial Technical Information Meeting

The most attractive ion exchange flowsheets for the recovery and partial purification of uranium is based on the sorption of uranyl ion as a chloride complex on anion resin and its elution with water. This step is attractive because of the low cost of elution and the preparation of uranium in a form relatively free from bulk ions. This product is suitable for either precipitation or electrolysis.

If it is desirable to recover both HF and uranium from MgF_2 scrap, the scrap is treated with H_2SO_4 , retorted to recover HF, and uranium recovered from the residue by ion exchange. Uranyl sulfate is extracted on anion resin from $MgSO_4$ solution. The sulfate on the resin is replaced by chloride using concentrated brine or 8 M HCl forming a uranyl chloride complex. The uranyl chloride complex is eluted with water as UO_2Cl_2 which can be precipitated as diuranate or reduced to UF_4 by the Excer process.

If HF recovery is not required, the MgF_2 scrap is leached with HCl and the uranyl chloride complex sorbed directly from the strong chloride solution (~ 8 M) containing suspended MgF_2 . Again the uranium is eluted with water as UO_2Cl_2 .

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Uranium may also be recovered from a carbonate leach by ion exchange. The principal advantage of ion exchange over precipitation is the elimination of a clarification step because the eluted product is carbonate solution similar to the original leach. In addition, dilute leach solutions can be concentrated to 25 g U/l.

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Recovery of U from Recycle Waste by Ion Exchange

By

I. R. Higgins

INTRODUCTION

Continuous ion exchange processes are being developed at ORNL for the recovery, concentration, and partial purification of crude uranium. The bulk of the studies have been concerned with ore leach pulps, but this paper will be confined to bomb liner scrap recovery studies.^{1,2,3,4} The ion exchange flowsheets have been designed to prepare feed for the Excer process.^{4,5,6} If electrolytic reduction by the Excer process is not desired, the partially purified ion exchange product may be precipitated as diuranate by standard methods. A separate paper has been included covering the electrolysis step.

ION EXCHANGE TREATMENT OF CHLORIDE LEACHED MgF₂ SCRAP

Scrap uranium is presently being recycled at FMPC by hydrochloric acid dissolution, filtration and precipitation. Using essentially the same dissolution procedure, ion exchange is proposed for elimination of the filtration step and for the preparation of a higher purity product. When MgF₂ scrap was dissolved in 8 M HCl, with NaClO₃ as an oxidant, magnesium was dissolved to 1.5 g/l and F to 0.8 g/l. Even in 8 M HCl fluoride has some affinity for the anion resin but is scrubbed out with fresh 8 M HCl, which is required anyway to displace contaminants in the void volume.

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The uranium is eluted with water. Product concentrations of UO_2Cl_2 of over 200 g U/l has been demonstrated in continuous operation in a Higgins contactor. If it is desired to precipitate at this point, alkali may be added. A NaU_2O_7 cake, prepared from UO_2Cl_2 and washed with water contained only 0.01 wt % chloride. If the Excer route is preferred, the UO_2Cl_2 is ready for electrolysis after adding HF .^{4,5,6}

The barren waste is used as a source of high chloride for feed makeup. Calcium oxide or CaCl_2 is added to prevent a buildup of SO_4 or F. A crude solid-liquid separation, with no washing, is sufficient to remove the CaF_2 or CaSO_4 since a bleed stream is necessary anyway (see Fig. 1).

ION EXCHANGE TREATMENT OF SULFATE LEACHED MgF_2 SCRAP

Magnesium fluoride scrap could be leached with sulfuric acid and only the uranium recovered, but if digested in HF distillation equipment, this valuable by-product would also be recovered. In either situation the uranium occurs in a MgSO_4 solution with varying amounts of MgF_2 as slurry depending on the completeness of the HF recovery. The anion exchange recovery of uranium is identical to that of sulfate ore leach, the uranium being sorbed as the sulfate complex. By displacing the sulfate with strong chloride, 5 M or greater, the uranium is eluted with water and treated as in the previous discussion (Sec. 3.0). The sulfate leach system has the advantage of a less expensive acid. No recycle of leach liquor is required, as in the chloride system, because uranyl sulfate is anionic in dilute solution. The sulfate system has the disadvantage

of continually going through a sulfate-chloride exchange on the resin, which reduces the overall production rate below what is possible with an all-chloride system (Fig. 2).

ION EXCHANGE TREATMENT OF CARBONATE LEACHED SCRAP

Mallinckrodt is presently using a Na_2CO_3 , NaHCO_3 , KMnO_4 leach of calcined MgF_2 bomb liner scrap. The final leach slurry is filtered and the uranium precipitated as diuranate. This carbonate leach material was tried on the 2-in. dia. Higgins contactor. The KMnO_4 was reduced to MnO_2 with H_2O_2 to prevent sorption of permanganate ion on the anion exchange resin. The MnO_2 and MgF_2 slurries were treated on 20-40 mesh resin with no indications of plugging.¹ Eluting systems were not thoroughly investigated but 1 M NaHCO_3 was found to be effective.

This carbonate cycle fits anion exchange very well, but this system does not have any great advantage over precipitation. Purification is not needed because carbonate dissolution is a purification step in itself. Concentration is not required because the feed and product solution strengths are essentially the same. The diuranate precipitation step is not avoided by using ion exchange. If filtration of the MgF_2 slurry, separation of traces of MgF_2 from the uranium solution, or loss of uranium by adsorption on the MgF_2 particle are difficult problems, the resin-in-pulp treatment would be of value. If the carbonate leach were used on very dilute uranium sources, ion exchange would serve as a recovery-concentration step (see Fig. 3).

PERFORMANCE OF A 2-in. HIGGINS CONTACTOR USING A CONTAMINATED
SULFATE LEACH AND THE STRONG CHLORIDE-WATER ELUTION SYSTEM

The high-chloride sorption and water elution system for treating uranium sources is presently being studied using a 2-in. dia. Higgins contactor. Synthetic sulfate ore leach or scrap feeds were prepared, containing recycle sulfate-chloride ion exchange wastes and electrolytic cell supernate from a previous Excer run containing UO_2F_2 and HF. The recovery of uranium was $>99.8\%$ when using 4 ft of Permatit SK-20-40 mesh resin loaded to 44 g U/l (see Fig. 4).

In the presence of a high concentration of chloride ion ($> 5 \text{ M}$), it is theoretically possible to displace sulfate equivalent for equivalent with chloride. A 3 ft column section was used for this purpose and proved to be too short. Further work also remains to determine the level to which sulfate must be reduced to prevent uranium losses. Nevertheless, from the approximate one equivalent capacity of the resin, the sulfate in solution has been reduced in three feet to 0.006 molar with a consumption of six equivalents of HCl (as 8 M), to 0.028 molar with 4 equivalents, and to 0.36 molar with three equivalents (5 M NaCl), see Fig. 5.

The water elution of uranium from resin loaded with uranyl chloride anion complex is very rapid and complete as compared to elution of a sulfate loaded resin with 1 M chloride. On dilution, the UO_2Cl_2 has essentially no affinity for the resin. The concentration of product that is withdrawn depends upon initial uranium concentration in the resin phase. The maximum product concentration that can be removed is the maximum loading capacity

of the resin in the strong chloride solution multiplied by 2.5, the void volume factor. When using 8 M HCl for scrubbing sulfate, uranium product concentrations of over $> 200 \text{ g U/l}$, as UO_2Cl_2 , have been achieved (see Fig. 6).

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Fig.1. Flowsheet for Recovery of Uranium from Bomb Liner Slag. Chloride Leach.

Fig. 2. Flowsheet for Recovery of Uranium and Anhydrous HF from Bomb Liner Slag.

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Fig. 3. Flowsheet for Recovery of Uranium from Bomb Liner Slag.
Carbonate Leach.

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Fig.4. Loading Column Height Required to Maintain Low Uranium Loss from Sulfate Leach. 593 012

Fig. 5. Elution of Sulfate from Uranyl-Sulfate-Loaded Resin with 8M HCl or 5M NaCl

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Fig. 6. Column Height Required to Elute Uranyl-Chloride-Loaded Resin with Water.

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