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Abstract

RECOVERY OF URANIUM FROM RECYCLE WASTES BY FLUORIDE VOLATILITY

by

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Industrial Technical Information Meeting

The present method of recovering uranium from the scrap obtained in the production of reactor fuel elements consists of obtaining a nitrate solution by dissolving or leaching, solvent extraction, and, finally, precipitation. An alternate method that has been investigated for scrap processing is fluoride volatility. It was found that reaction of MgF_2 slag with elemental fluorine at $400^\circ C$ volatilized 99% of the contained uranium, provided that good gas-solid contact was obtained. Based on these laboratory results, a process which consists of grinding, screening, fluorinating with fluorine gas at $400^\circ C$ in an agitated reactor, and collecting the product UF_6 in a cold trap appears to be an attractive method for treating the scrap from the UF_6 and UF_4 reduction steps. The oxide and metal scrap and HNO_3 pickling liquor would require chemical conversion to UF_4 before fluorination, and for this reason the volatility method does not appear to be greatly simpler than the present aqueous method for this type of scrap. (auth)

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INTRODUCTION

Relatively large quantities of uranium-containing scrap are produced in the reduction of uranium to the metal and in the fabrication of this metal into reactor fuel elements. This scrap consists of uranium in a variety of chemical forms and containing a variety of contaminants. The present method of recovering uranium from this scrap consists of obtaining a nitrate solution by dissolution or leaching, solvent extraction and precipitation. This wet chemistry method has the outstanding advantage that it can successfully handle the large variety of scrap that is produced. However, it has the disadvantage of requiring costly chemical conversions to return the salvaged uranium to either the metal production line or to a diffusion plant.

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An alternate method that appears attractive for uranium scrap recovery is fluoride volatility. Basically this method has the advantage that the product, UF_6 , may be returned directly to either the metal production line or to a diffusion plant. For some forms of the scrap, for instance, reduction slag, this method would represent a large improvement over the wet method, but for others, for example HNO_3 pickling liquor, extensive preparation would be required before fluorination to UF_6 is possible.

The nature of uranium-containing scrap from the production of a typical low enrichment reactor fuel element is given in Table 1. This table lists the source of the scrap and indicates the present Y-12 processing method. From the standpoint of uranium recovery the scrap can be divided into two classes: the fluoride-containing scrap from the UF_6 and metal reduction steps, and the essentially fluoride free scrap from the metal handling steps. This paper presents a general discussion of the applicability of fluoride volatility to the scrap recovery problem and the results of laboratory studies on the fluorination of metal reduction slag.

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Table 1. Nature of Scrap

Source of Scrap	Nature of Scrap	Y-12 Processing Method
UF ₆ reduction	Dust collector residues and slurries	Complex, leach, extract, ppt.
	Contaminated green salt	Complex, leach, extract, ppt.
Metal reduction	Slag and liner	Muffle, mill, complex, leach, extract, ppt.
	Miscellaneous residues	Complex, leach, extract, ppt.
Casting	Black oxide	Dissolve, extract, ppt.
	Molds and graphite	Leach, extract, ppt.
	Sludge	Leach, extract, ppt.
Slabbing	Black oxide and $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$	Dissolve, extract, ppt.
Fuel fabrication plants	Oxide and metal	Dissolve, extract, ppt.
	Rolling mill oxide	Dissolve, extract, ppt.
	HNO ₃ pickling liquor	Extract, ppt.

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FLUORINATION OF MgF_2 SLAG

Several investigators have studied the feasibility of recovering uranium from magnesium fluoride slag by a fluoride volatility process. Tests were made with ClF_3 , BrF_3 and F_2 as fluorination agents. The use of ClF_3 was studied at Mallinckrodt.⁽¹⁾ In one series of laboratory tests with slag that had been previously hydrofluorinated (Table 2), about 94% of the uranium was recovered in 30 min at 350-420°C with a 50-100 fold excess of ClF_3 . However, this recovery is not high enough for slag containing more than 1% uranium, since an acceptable residual content is only 0.05%.

In a similar set of tests with slag that had not been hydrofluorinated and with the ClF_3 diluted with helium, increasing the fluorination temperature increased the uranium recovery up to 380°C; above this temperature no increase in uranium recovery was noted up to 620°C. No data were obtained on the consumption of ClF_3 in these experiments. In none of these tests was adequate uranium recovery obtained in 60 min with a 35-fold excess of ClF_3 . These scouting experiments with ClF_3 were discontinued before the suitability of this fluorinating agent was firmly established.

The use of elemental fluorine for volatilizing UF_6 from MgF_2 slag has been studied on a laboratory scale at Oak Ridge National Laboratory⁽²⁾ and Mallinckrodt.⁽¹⁾ In the tests conducted at ORNL, reaction of a thin layer of slag (0.05 in.) with fluorine gas volatilized 97% of the uranium in only 0.05 hr at 500°C (Table 3). Increasing the reaction time to 3 hr

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Table 2. Fluorination of MgF_2 Slag with ClF_3

Slag previously hydrofluorinated; screen analysis (wet): 3% of +200 mesh; 13% of -200 to +325 mesh; balance, -325 mesh

Reacted for 30 min with 50-100 fold excess ClF_3

Temperature (°C)	U in Slag (Wt %)	
	Before	After
350	1.80	0.098
420	0.84	0.048
350	0.90	0.061
350	1.70	0.19

Untreated slag; screen analysis (dry): 56% of +200 mesh; 15% of -200 to +325 mesh; balance, -325 mesh

Reacted for 60 min with a mixture of helium and ClF_3 ($He/ClF_3 = 2/1$), 35-fold excess ClF_3

Temperature (°C)	U in Slag (Wt %)	
	Before	After
100	1.8	0.92
190	1.8	0.42
310	1.8	0.24
380	1.8	0.17
500	1.8	0.19
620	1.8	0.17

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Table 3. Fluorination of MgF_2 Slag with F_2

Initial U concentration in slag, 1.5-2.0%

0.05-in. thick bed of slag reacted with F_2

Time (hr)	Temperature (°C)	Particle Size (mesh)	Uranium in Residue (%)
0.05	500	-100	0.049 ^a
0.5	500	-100	0.048 ^b
1.0	500	-100	0.040
3.0	500	-100	0.020 ^a
3.0	370	-100	0.025 ^b
3.0	500	-35, +60	0.17
3.0	500	Unclassified	0.16
3.0	500	-60, +100	0.11

^a Average of three runs.

^b Average of two runs.

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reduced the residual uranium in slag of -100 mesh particle size to about 1% of the initial value of 1.5-2.0 wt %. In two other tests a reaction temperature of 370°C was equally effective. Uranium could not be adequately recovered with slag of particle size greater than 100 mesh. Also volatilization of uranium was not adequate when fluorine was passed over a static bed of ground slag with a bed depth of 0.5-1.5 in. This was attributed to the heavier UF_6 gas collecting in the lower part of the bed and preventing good contact with the fluorine.

These results indicate that it is possible to recover uranium from MgF_2 bomb-reduction slag by reacting with elemental fluorine at 370°C provided that the slag is ground to pass through a 100 mesh screen and provided that the slag is agitated to ensure good contact with the reacting gas.

The use of liquid BrF_3 as a fluorinating agent was tried in two experiments at Argonne National Laboratory⁽³⁾ by contacting slag with liquid BrF_3 at the relatively low temperature of 125°C for 6 hr. Uranium recovery was greater than 95%.

APPLICATION OF FLUORIDE VOLATILITY TO SCRAP PROCESSING

A schematic flowsheet for uranium recovery from MgF_2 slag by reacting with elemental fluorine is shown in Fig. 1. Fluorine was selected in place of ClF_3 or BrF_3 because of the comparative ease of separating F_2 and UF_6 and recycling the F_2 . In the case of the interhalogen fluorinating agents, fractional distillation or an equally complicated step would be

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required to separate the fluorinating agent from the UF_6 . The process consists of grinding and screening the scrap to less than 100 mesh to ensure that intra-particle diffusion does not limit the uranium recovery, reacting with fluorine gas at $400^{\circ}C$ to form volatile UF_6 in an agitated reactor to ensure good gas-solid contact, collecting the UF_6 in a cold trap, and recycling the excess F_2 to the fluorinator. While this process has been tested only in laboratory scouting experiments, it has been shown to be chemically feasible in the case of the MgF_2 slag and liner material. The fluoride-containing scrap from the UF_6 and metal reduction steps could also be processed along with the slag without extensive pretreatment.

The oxide scrap from the casting, slabbing, and fuel-fabrication steps would be converted to UF_6 by contact with fluorine at $400-500^{\circ}C$. Reduction to UO_2 and hydrofluorination prior to fluorination would probably be preferable. The uranium contained in the nitric acid pickling solution might be precipitated, burned to the oxide, reduced to the dioxide, and hydrofluorinated to UF_4 , and the uranium recovered and separated from impurities by fluorination to UF_6 in this process. It is obvious that in this particular case the present process, which uses solvent extraction to separate the uranium from impurities and then goes through the identical chemical conversions, is certainly as simple. The aqueous chemical route would also be just as convenient for solutions obtained in leaching uranium from the mold and graphite material, and in acid dissolution of the metal and oxide scrap. More development work will be required to establish optimum operating conditions for the slag

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process and the pretreatment required to obtain maximum recovery with a minimum fluorine consumption. Hydrofluorination prior to fluorination may drastically reduce the consumption of expensive fluorine gas. No attention has been given to the recycle of unused fluorine. Undoubtedly, volatile impurities will build up in the recycled gas and will require a disposal system.

From the standpoint of equipment this process introduces no novel problems. Engineering development certainly would be required to establish the best design and operating procedure for the fluorinator, and it may be necessary to use a cyclone separator and filter to prevent entrained solids from being carried over with the product. Suitable materials of construction are available in the high-nickel-base alloys, such as inconel or monel. Operation of the process at essentially atmospheric pressure throughout would probably be most practical in order to avoid in-leakage of air into the system, and to minimize the out-leakage of fluorine and UF_6 .

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