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UNITED STATES ATOMIC ENERGY COMMISSION

**THE ABSORPTION OF FLUORINE AND URANIUM
HEXAFLUORIDE BY SODIUM CARBONATE
SOLUTIONS**

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1946

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Appendix C
CHAPTER 11.

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THE ABSORPTION OF FLUORINE AND URANIUM HEXAFLUORIDE BY SODIUM CARBONATE SOLUTIONS.*

George G. Joris and Charles D. Compton (Princeton University)

INTRODUCTION

Complete removal of fluorine from waste gases also containing uranium hexafluoride was the object of the researches described in this chapter. In the proposed process, the uranium hexafluoride fed to the fluorine scrub tower was to remain in solution and the fluoride ion was to be efficiently precipitated. Preliminary work was carried on by The Kellogg Corporation laboratory and was later transferred to the Johns Hopkins University.⁽¹⁾ The program at the latter institution was interrupted before completion and work on the process was then transferred to the Princeton University group, where it was completed.

Attention was given at Johns Hopkins to two possible processes:

- (a) Addition of peroxide to the caustic solution for complete solution of uranium in the form of a soluble peroxy complex.
- (b) Use of a solution of sodium carbonate instead of caustic solution for the absorption of fluorine and uranium hexafluoride with formation of sodium fluoride and a soluble uranium carbonate complex.

The first process was discarded because of the instability of the uranium peroxy complex in the alkaline absorption solution. Attention was therefore focused on the second process and by the time the work at Johns Hopkins was suspended, it had been established that fluorine and uranium hexafluoride would dissolve in sodium carbonate solutions and that regeneration of the sodium carbonate could be achieved by addition of magnesium oxide.

* This chapter is based on report A-3889, January 24, 1946 by the same authors and with the same title.

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However, under certain, undefined circumstances, in the precipitation of fluoride ion with magnesium oxide, uranium was precipitated along with the magnesium fluoride.

The pilot plant system in which the process was tested is described in section 2 of this chapter. Before this apparatus was used a series of static experiments were carried out in order to obtain preliminary information on the efficiency of sodium carbonate solution as an absorbing medium and that of magnesium oxide for the removal of fluoride and the regeneration of sodium carbonate.

The principle of the proposed system is that the fluorine and uranium fluoride are absorbed in a tower by sodium carbonate solution. The chemistry of the absorption is not thoroughly understood. The fluorine is presumably converted to fluoride ion with the simultaneous formation of bicarbonate and peroxide. The uranium hexafluoride is converted into the soluble uranium tricarbonate complex, presumably $UO_2CO_3(Na_2CO_3)_2$, or into the soluble uranium peroxy complex and into fluoride ion with simultaneous formation of some bicarbonate. The magnesium oxide in water slurry is thoroughly mixed with the spent tower solution, fluoride ion is precipitated as magnesium fluoride and bicarbonate ion is converted to carbonate ion. The magnesium oxide in excess and the magnesium fluoride are removed by settling.

The program was directed towards the investigation of the following factors:

- (1) The selection of the most suitable type of magnesium oxide.
- (2) The solubility of the uranium complex in sodium carbonate solutions.
- (3) The precipitation of the fluoride ion.
- (4) The conversion of the bicarbonate to carbonate.
- (5) The settling rate of the slurry.

For convenience, the discussion of the work will be divided into static experiments and cyclic system experiments.

1. Static Experiments

1.1 ~~(1)~~ The Selection of the Magnesium Oxide

Three grades of magnesium oxide manufactured by the Westvaco Chemical Company were investigated. The three grades were available in quantities that would be necessary in plant operation and were described by Westvaco as follows:

- (a) Adsorptive Powdered Magnesia - No. 2642
- (b) Adsorptive Granular Magnesia - No. 2652-S
- (c) Select Grade Magnesia - No. 2665 (Powdered)

In order to investigate the relative effectiveness of these magnesium oxides for the removal of fluoride ions the following experiments were carried out.

A solution was prepared which contained 40 grams (0.47 moles) of NaHCO_3 and 20 grams (0.47 moles) of NaF per liter. This solution should closely approximate that obtained when a 5% Na_2CO_3 solution has absorbed fluorine until it has been completely converted into NaHCO_3 , assuming an equimolar relationship between fluoride and bicarbonate. Five hundred cc. of this solution were placed in a 1000 cc. round-bottom flask equipped with mechanical stirrer and mercury seal. To this was added 14.25 g. of magnesium oxide (three times the theoretical amount necessary to precipitate the fluoride ion present) and the slurry stirred. Samples for analysis were removed from time to time. The comparative results for the three magnesium oxide samples are given in Table I.

TABLE I

Time (hrs.)	No. 2665 MgO		No. 2642 MgO		No. 2652-S MgO	
	F ppm.	pH	F ppm.	pH	F ppm.	pH
0	9100	8.9	9100	8.6	9100	8.6
0.5	1700	10.2	--	10.3	7500	--
1.5	1540	10.4	1610	--	7320	9.5
3	--	--	1622	--	--	--
8	1162	10.4	--	10.7	--	--

The results in Table I indicate that the No. 2665 and No. 2642 magnesium oxides are superior to the No. 2652-S magnesium oxide in effectiveness of the removal of fluoride ions. Since the No. 2665 magnesium oxide is much lower in cost than either of the other two types, this magnesium oxide was selected for future use. It should be noted that the rate of fluoride ion removal in these experiments is considerably greater than that to be expected in the plant, since the MgO concentration is much greater than that in the plant regeneration tank.

1.2 (2) The Solubility of the U Complex

(a) To determine what effect the magnesium oxide has on the solubility of the U complex a solution was prepared by adding sufficient solid U-carbonate complex to a 5% Na_2CO_3 solution to furnish about 4000 ppm. of U. To 500 cc. of this solution was added 14.25g. of No. 2665 magnesium oxide (three times the theoretical) and the slurry stirred. Samples for analysis were removed from time to time as indicated.

The results are indicated in Table II.

TABLE II

Sample	Elapsed time (hrs)	U ppm
0	0	4010
1	1/2	3930
2	6	3960
3	23	3960
4	72	3910
5	101	3910
6	146	4000
7	170	4000

These results indicate that magnesium oxide will not cause precipitation of U.

(b) To investigate the solubility of U during the regeneration step a run was carried out wherein fluoride ion was precipitated in the presence of U. A solution was prepared which closely approximates that probably obtained when a 5.5% Na_2CO_3 solution has absorbed U to a concentration of about 4000 ppm. and fluoride ion to a concentration of about 8600 ppm. assuming that bicarbonate ion is formed in equimolar ratio with fluoride ion. To 500 cc. of this solution was added 14.25g. of No. 2665 magnesium oxide (three times the theoretical). The solution was

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stirred, and samples for analysis removed from time to time. The results are presented in Table III.

Since a 10% sodium carbonate system will probably prove to be preferable to a 5% system, the same experiment was carried out in a solution which represents that obtained when U is absorbed to 4000 ppm. and fluoride to 8600 ppm. by a 10% sodium carbonate solution, assuming that bicarbonate ion is formed in equimolar ratio with fluoride ion.

The results are also presented in Table III.

TABLE III

Time hrs.	5.5% Na ₂ CO ₃ system			10% Na ₂ CO ₃ system		
	F ppm.	U ppm.	pH	F ppm.	U ppm.	pH
0	8600	4030	9.3	8703	4080	9.8
0.5	1620	3960	10.4	2377	4010	11.0
1.5	1349	4010	10.7	1330	4010	11.3
3	1225	--	11.0	1814	4080	11.6
8	1219	4000	11.3	1340	4110	11.7
24	1365	4010	11.5	1997	4150	11.7
48	1108	4000	--	1490	--	11.8
72	1260	4010	11.5	--	--	--
96	998	4100	11.4	--	--	--
120	--	--	--	1264	4100	12.1
169	632	4000	11.8 (")	1415	4190	11.7 (?)

The results in Table III indicate that when fluoride ion is precipitated by magnesium oxide from a solution highly concentrated in U and fluoride ion, and containing bicarbonate ion in equimolar ratio with fluoride ion, U in concentration of at least 4000 ppm. should remain in solution.

(c) When magnesium oxide is continuously added to a solution in which there is initially considerably less than an amount of bicarbonate equivalent to the fluoride ion concentration, the pH will rise to a high value. The U-carbonate complex solubility under such circumstances becomes less. A solution was prepared containing 4000 ppm. U, 8400 ppm. fluoride ion, an amount of sodium bicarbonate equivalent to 4200 ppm. of fluoride ion, and sufficient sodium carbonate to make the carbonate concentration equivalent to a 10% sodium carbonate system. The results of this experiment are presented in Table IV.

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TABLE IV

Time (hrs.)	F ppm.	U ppm.	pH
0	8434	3970	10.3
0.5	3473	3860	12.2
1.5	2754 (?)	3800*	12.5
3	3079 (?)	3800*	12.6
8	3422	3800*	12.7
24 ⁺	3208	2030	12.7
32	3158	1660	12.8
48	3424	1470	12.7
72	2692	1280	12.7

* These analyses were made within 2 hours after the samples were removed from the reaction flask. A yellow precipitate formed overnight indicating subsequent precipitation of U.

⁺ At this point the slurry insoluble was observed to be orange in color instead of the usual white.

The results in Table IV indicate that with continuous addition of magnesium oxide to a system containing initially 4200 ppm. of fluoride ion for which there is no bicarbonate, the pH will climb to 12.7 and U will precipitate. It had been found at the Johns Hopkins University that under similar conditions such U precipitation had been observed. No pH data had been given, however; correlation with this important factor is not possible.

This U precipitation has been found to be reversible. After the reaction had been proceeding for 72 hours there were 160 cc. of slurry remaining. To this slurry was added 2g. of NaHCO_3 and stirring continued for 6 hours. The slurry insoluble remained orange in color. Two more grams of NaHCO_3 were added. After 8 hours the slurry insoluble was again white and the supernatant liquor was again the characteristic canary yellow. An analysis of the supernatant liquid revealed that there were 3950 ppm. of U in solution indicating complete solution. The pH of the supernatant solution was 10.9.

(d) The solubility of U appears to be influenced by the pH of the solution more than by any other factor. To determine the equilibrium U concentration at the high pH range, solutions of U at various pH's were prepared by adding 1 M NaOH to a solution containing 5% Na_2CO_3 and 4000 ppm. of U. These solutions were allowed to stand for 2 days, and samples of the clear supernatant of each solution were then analyzed for U. The results are given in Table V.

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TABLE V

Sample	pH	U ppm.	remarks
1	11.6	4090	no precipitate formed
3	11.8	4100	" " "
5	12.2	4090	" " "
6	12.4	4040	" " "
4A	12.5	3940	precipitate formed
7	12.6	3420	" "
8	12.7	1530	" "

Table V indicates that the U complex will remain in solution to the extent of 4000 ppm. of U up to a pH of 12.4. At higher pH's the U will precipitate.

1. 3. The Removal of Fluoride Ion.

(a) The results given in Tables III and IV, indicate that the magnesium oxide will reduce the fluoride ion concentration effectively. An equilibrium fluoride ion concentration is reached which depends on the pH of the system as would be expected. On the basis of these static experiments it appears that at pH of about 11.5 this is about 1000 ppm., at pH of about 12.0 about 1300 ppm., and at a pH of about 12.7 about 3200 ppm.

(b) While at the plant it is intended to feed magnesium oxide into the system at a rate sufficient to supply three times the theoretical amount needed to react with the fluorine introduced into the system in a given time interval, the concentration of magnesium oxide in the regeneration tank at any given time will be considerably less than this, perhaps as low as one-fiftieth of this. In the static experiments reported thus far, three times the theoretical amount of magnesium oxide was present in the reaction mixture. While such a concentration furnished desirable values of pH, U solubility and fluoride ion equilibrium, the rate of fluoride ion precipitation was increased considerably over that to be expected in the plant.

To determine the effect of a reduced concentration of magnesium oxide on the rate of fluoride ion removal the following experiment was carried out. A solution was prepared containing 4000 ppm. of U, 8600 ppm. of fluoride ion, sufficient NaHCO_3 to furnish a 1 to 1 molar ratio with the fluoride ion present, and sufficient Na_2CO_3 to correspond to a 10% NaCO_3 system. To 500 cc. of this solution 1.25g. of Westvaco No. 2565 magnesium oxide were added. The mixture was stirred, and samples removed for analysis as indicated.

The results are indicated in Table VI.

TABLE VI

<u>Time (hrs.)</u>	<u>F ppm.</u>	<u>U ppm.</u>	<u>pH</u>
0	8703	4080	9.8
0.5	6994	4090	10.1
1.5	6720	4050	10.1

The results in Table VI indicate that the reduced concentration of magnesium oxide results in a decreased rate of fluoride ion removal, as would be expected. Further static experiments of this type were discontinued at the time, attention was transferred to the cyclic system.

(c) In order to show that the presence of bicarbonate ion in the reaction mixture is an important factor in the rate of fluoride ion removal, the following experiment was carried out. A solution was prepared which contained 50 grams of sodium carbonate and 23 grams of sodium fluoride per liter. To 500 cc. of this solution contained in a 1 liter flask were added 20 grams of Westvaco No. 2665. Select grade magnesium oxide and the solution was thoroughly stirred. Samples for analysis were removed from time to time. The results are presented in Table VII.

TABLE VII

<u>Time (hrs.)</u>	<u>F ppm.</u>	<u>pH</u>
0	10400	11.40
0.5	--	11.35
1.5	8750	11.40
3.	7850	--
6	7823	--

When these results are compared with those presented in Table I, it can be readily seen how the presence of bicarbonate ion accelerates the removal of fluoride, and makes possible a reduction to a much lower level.

These results are in good general agreement with the results of similar experiments carried out at Johns Hopkins. It was found there

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that in the absence of bicarbonate 3.2g. of MgO reduced the fluoride content of 300 cc. of solution from 7000 ppm. to 4900 ppm. in 6 hours. In the presence of bicarbonate the comparable rate was a reduction from 7000 ppm. to 910 ppm. in one hour.

1.4
1.4.1 The Conversion of Bicarbonate to Carbonate

(a, A solution was prepared containing 20g. (0.47 moles) of NaF per liter and 40g. (0.47 moles) of NaHCO₃ per liter. This solution represents a 5% Na₂CO₃ system which has absorbed sufficient fluorine to convert all the carbonate present to bicarbonate, assuming that bicarbonate ion and fluoride ion are formed in equimolar ratios. To 500 cc. of this solution 14.25g. of No. 2655 magnesium oxide was added (three times the theoretical) and the slurry stirred. Samples were taken at the times indicated in Table VIII where the results are presented.

TABLE VIII

Elapsed Time (hrs.)	F ppm.	pH	(CO ₃ ⁻) [*]	(HCO ₃ ⁻) [*]	unaccounted [*]
0	9100	8.9	0	100	0
0.5	1770	10.2	63	28	9
1.5	1540	10.4	66	23	11
8	1162	10.4	71	16	13

*values in these columns are percentages of the carbonate originally present.

(b) A second experiment was carried out, similar in all details to the one described above, except that the original solution contained in addition 50g. of Na₂CO₃ per liter. This solution represents a 10% sodium carbonate system which has absorbed fluoride ion to a concentration of about 8700 ppm. The results of this run are given in Table IX.

TABLE IX

Elapsed Time (hrs.)	F ppm.	pH	(CO ₃ ⁼)*	(HCO ₃ ⁼)*	unaccounted*
0	8670	9.9	54	46	0
0.5	--	10.6	82	14	3
1.5	2307	10.7	85	11	4
3	2392	10.8	--	--	--
8	--	10.8	--	--	--
25	830	11.1	94	2	4
48	821	11.2	97	0	3

* values in these columns are percentages of the carbonate originally present.

The results in Tables VIII and IX indicate that the conversion of the bicarbonate by the MgO is sufficiently effective. The unaccounted is possibly carbonate precipitated as MgCO₃. Such precipitation should be less as the pH of the system increases. Comparison of Tables VIII and IX indicates that such is the case. X

(c) In a third experiment, the effect was determined of the addition of a similarly large excess of magnesium oxide to a static reaction mixture containing initially 2000 ppm. of fluoride ion for which there is no bicarbonate. A solution was prepared containing 9000 ppm. fluoride ion, an amount of sodium bicarbonate equivalent to about 6000 ppm. fluoride ion, and sufficient sodium carbonate to furnish a total carbonate concentration equivalent to a 10% sodium carbonate system. To 500 cc. of this solution 14.25g. of Westvaco No. 2665 magnesium oxide were added, the mixture stirred, and samples for analysis removed from time to time. The results are presented in Table X.

TABLE X

Time (hrs.)	F ppm.	pH	(CO ₃ ⁼)*	(HCO ₃ ⁼)*	unaccounted*
0	9042	10.0	63.9	36.1	0
0.5	1936	11.7	97.0	0	3.0
1.5	2115	11.9	--	--	--
3	--	12.0	--	--	--
8	1626	12.0	--	--	--
24	1809	12.0	98.6	0	1.4
48	1739	12.0	--	--	--

* The values in these columns represent percentages of the total carbonate initially present.

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The results reported in Tables VIII and IX indicate that in the conversion of HCO_3^- to CO_3^{2-} by MgO not all of the original carbonate content was accountable. While the analytical accuracy is perhaps no better than about 3%, the results did suggest a possible loss of carbonate from the system. The amount of such unaccountable carbonate became less with increasing pH. On the basis of a 10% sodium carbonate system the unaccountable was found to be about 6% at a pH of 10.4 and about 4% at a pH of about 11.0. The results in Table X indicate that at a pH of 12.0 it is less than 2%.

1.5. The Settling Rate of the Slurry

Preliminary experiments indicated that the slurries remaining at the end of the experiments (169 hours) reported in Table III will settle in about 30 minutes. Further work was discontinued until experiments using the cyclic system were begun.

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2.0 Experiments in Cyclic System

INTRODUCTION

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PM.

The preliminary static experiments indicated that:

(1) Westvaco magnesium oxide No. 2665 will probably be efficient for fluorine removal and sodium carbonate regeneration in plant operation.

(2) The pH of the absorption solution is a critical factor in the solubility of the U-compounds in the solution.

(3) The magnesium oxide and magnesium fluoride will settle from the solution sufficiently quickly.

Many uncertain aspects remained, however. For example, assumptions were made in the preparation of the static reaction mixtures concerning the chemistry of absorption of fluorine and uranium hexafluoride. In general the uncertain aspects which remained to be investigated before the general workability of the system could be demonstrated included the following:

(1) The operating pH and its effect.

(2) The rate of fluoride ion removal.

(3) The effect of U-peroxide formed during the absorption of fluorine by a solution containing uranium.

(4) The rate of slurry settling.

(5) The effect of suspended magnesium oxide in the absorption tower on the solubility of U-compounds.

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2. | Description of the Cyclic System

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sketched in figure 1.

| The apparatus is

The absorption tower consisted of a 65 mm. glass tower four feet high packed with 1/4 inch glass Raschig rings. The gas inlet at the bottom was of nickel. The fluorine and uranium hexafluoride were introduced at this point diluted well with nitrogen. A 10% sodium carbonate solution flowed under gravity into the top of the column, and drained at the bottom into a 4 liter bottle. A magnesium oxide - water thick paste were fed into this flask, and the resulting slurry was continuously stirred. The solution drained from here into a settling tank. The solution was pumped from the top of the opposite end of the settling tank by a centrifugal pump up to a reservoir, from which it flowed by gravity into the column. The liquid flow was regulated by a needle valve between the reservoir and the column. The magnesium oxide was introduced at a constant rate by forcing a thick water paste of known oxide content from a horizontal tube by a mechanically driven piston. Samples for analysis were removed from the settling tank next to the outlet tube.

Data on the System

Volume of liquid	50 liters
Liquid flow rate	190 cc/min
Time for complete liquid cycle	4.5 hours
Volume of settling tank	39 liters
Hold-up time of the settling tank	3.5 hours
Volume of the regeneration flask	4 liters
Hold-up time of the regeneration flask	20 minutes

Experiment No. 1

The purpose of this experiment was to determine the rate of reduction of a peak fluoride ion concentration in the cyclic system and to determine the equilibrium fluoride ion concentration of the system.

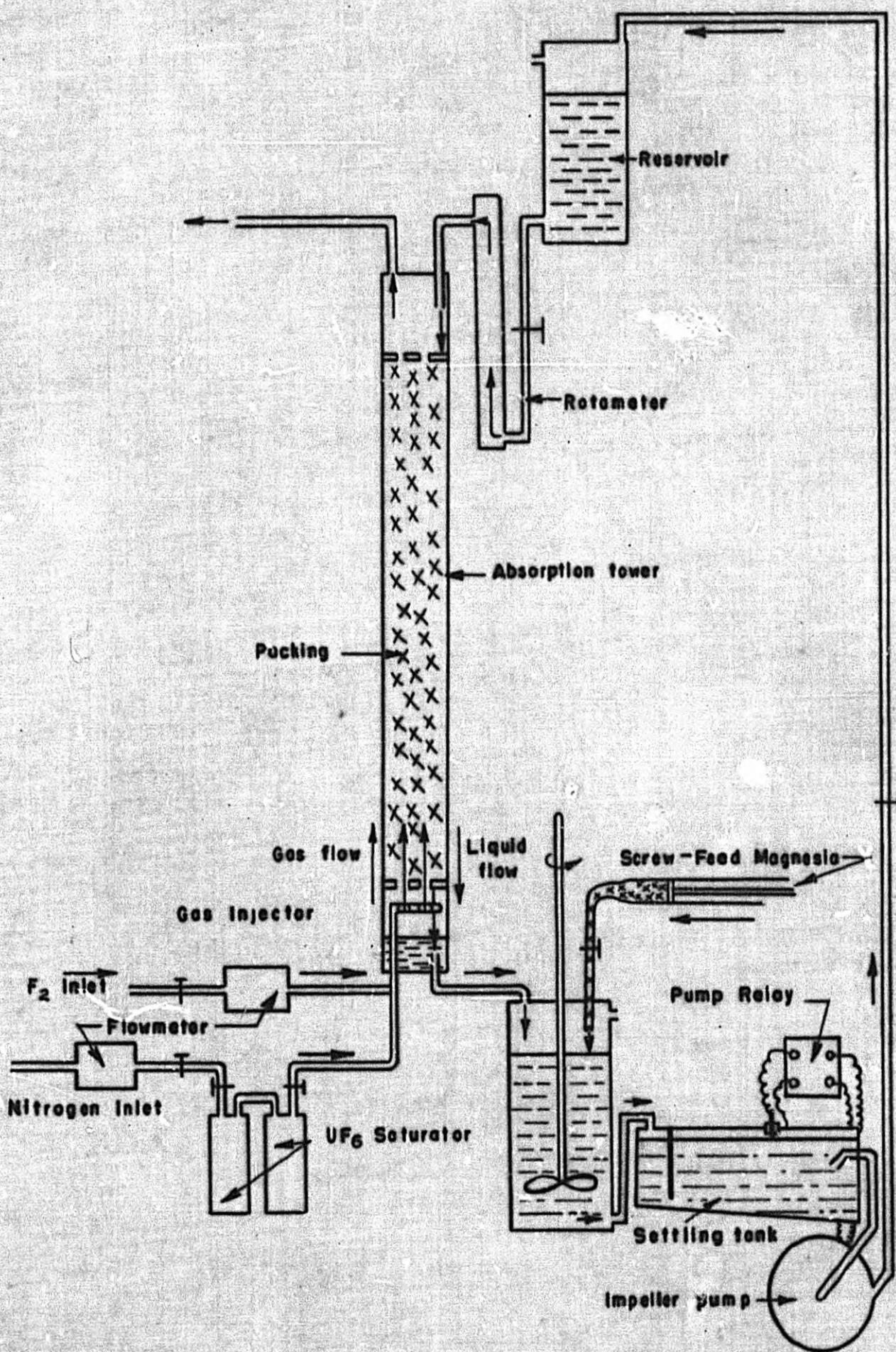
The absorption solution was initially 10% sodium carbonate by weight. During preliminary apparatus testing, some fluorine and some magnesium oxide had been introduced into the system.

Over a period of about 20 hours a nitrogen mixture containing about 5% fluorine was introduced to build up a fluoride concentration

FIG. 1

CYCLIC SYSTEM FOR UF_6 AND FLUORINE ABSORPTION

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of about 5300 ppm. The nitrogen flow was 2800cc/min. Because of metering and other apparatus difficulties the amount of fluorine added is not known with any certainty. Some magnesium oxide was introduced during this time but this was discontinued in order to increase the fluoride ion concentration more rapidly.

When the fluoride ion concentration had reached 5300 ppm, the continuous addition of fluorine was stopped. Addition of fluorine was then resumed at the rate of 1040 cc. per hour added over a period of 10 minutes during each hour. Addition of magnesium oxide was also resumed at this point and added continuously at the rate of 5.64 g/hour (three times the amount needed to precipitate the fluorine added during the same time). Samples for analysis were taken at the settling tank exit every few hours, and the concentration of F^- , CO_3^{2-} and HCO_3^- and the pH determined.

Thirty three hours after the start of the continuous magnesium oxide feed the fluorine addition was stopped, but the oxide addition continued. The run was halted at the end of 45 hours because of a breakdown in the magnesium oxide feed mechanism. The results from the beginning of the magnesium oxide feed are presented in Table XI.

TABLE XI

(1) Total time (hours)	pH	Total CO_3^{2-} mols/l	CO_3^{2-} mols/l	HCO_3^- mols/l	F^- mols/l	F ppm.
0	10.9	1.06	0.98	0.08	0.28	5295
4	10.9	1.06	0.99	0.07	0.23	4404
9.5	11.0	1.05	1.00	0.05	0.20	3743
14	11.0	1.05	1.00	0.05	0.17	3207
19	11.1	1.05	1.01	0.04	0.17	3253
24	11.1	1.05	1.02	0.03	0.19	3592
29	11.1	1.05	1.02	0.03	0.17	3260
34 (2)	11.2	--	--	--	0.16	3089
39	11.1	1.05	1.02	0.03	0.17	3321
45 (3)	11.2	1.06	1.04	0.02	0.16	2980

(1) Total time to nearest half hour from the start of magnesium oxide addition.

(2) Fluorine stopped at end of 33 hours.

(3) Run stopped because of magnesium oxide feed mechanism breakdown.

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The results in Table XI indicate that should fluoride ion accumulate in the system to the extent of 5300 ppm., such a peak value should be removed in about 14 hours if magnesium oxide and fluorine addition to the system approximates amounts proportional to those of the run. The equilibrium concentration of the fluoride ion appears to be around 3000 ppm. The total carbonate content (carbonate plus bicarbonate) of the system remains constant. The amount of bicarbonate is unaccountably low, being only about one-third the amount to be expected on the basis of a one-to-one molar ratio with the fluoride ion present.

Experiment No. 2

The purpose of the run was sixfold. First it was desired to obtain information as to the solubility of the U compounds during fluoride ion precipitation. Secondly, the effect of the U peroxide formed during fluorine addition to a U solution was to be observed. Thirdly, it was desired to check the rate of fluoride ion removal and its equilibrium value in the presence of the U compounds. Fourthly, it seemed desirable to check the fluoride-bicarbonate molar ratio when fluorine is absorbed by a sodium carbonate solution in the absence of any magnesium oxide. Fifthly, the effect of reduced MgO feed was to be tested. And lastly, the pH during the various phases of the experiment was to be determined.

The general plan of the run was to add fluorine (1: about 5% nitrogen mixture) to the 10% sodium carbonate solution in the system until the fluoride content rose to about 4000 ppm. At this time the fluoride-bicarbonate ratio could be checked. Addition of UF_6 would then be begun (in mixture with nitrogen) until the U concentration reached 4000 ppm. or higher. At the same time fluorine would be added intermittently and magnesium oxide continuously. Such fluorine and magnesium oxide addition would be continued after U addition had been stopped. The rate of fluoride ion removal and the equilibrium fluoride ion concentration could then be determined. When the fluorine ion concentration had been reduced to a suitably low value, the addition of fluorine would be stopped. The addition of MgO would continue, and the effect on the pH of the system and the solubility of the U compounds determined. Finally, the fluorine addition would be resumed and the MgO feed rate reduced. The constancy of the fluoride ion concentration under such conditions could then be determined.

16.

PART VIII

24.

2.2 The Introduction of Fluorine to a Peak of About 4000 ppm.

Fluorine diluted with nitrogen was introduced at a rate somewhat less than 4.5 liters/hour for 30 hours. The nitrogen flow rate was 168 liters/hour. During this time no magnesium oxide was introduced into the system. The system solution was circulated at the rate of 190 cc./min. Samples for analysis were taken from the outlet end of the settling tank at the times indicated. The results are presented in Table XII.

TABLE XII

Total time (hours)	F ppm.	F mol/l	Total carbonate mols/l	CO ₃ ⁼ mols/l	HCO ₃ ⁼ mols/l	pH	mols F ⁻ mols HCO ₃ ⁼
0	--	--	1.07	1.07	0.00	11.5	--
4	1354	0.071	1.07	1.06	0.02	11.5	3.5
9.5	1626	0.086	1.04(1)	1.01(1)	0.03	11.4	2.9
12.5	2173	0.114	1.07	1.03	0.04	11.3	2.9
19	3057	0.161	1.06	1.00	0.06	11.2	2.7
30	4279	0.225	1.08	1.00	0.08	11.0	2.8

(1) Due to analytical error these values are known to be low.

On the basis of a 4.5 l/hour fluorine flow rate and an estimated volume of 50 liters for the system the concentration of fluoride is calculated to be 4600 ppm. Since the flow was known to be somewhat less than 4.5 l/hour, the fluorine balance appears to be as close as can be calculated from the data.

The ratio of the mols of F⁻ to the mols of HCO₃⁼ appears to remain rather constant at slightly under 3 to 1 for a reason yet to be explained. The total carbonate content remained constant.

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2.3 The Introduction of UF_6

During a period of 14 hours sufficient UF_6 was introduced into the system to accumulate a U content of 5700 ppm. This indicates that UF_6 was introduced at the rate of slightly more than 20g. per hour, or at about 1.92 l. per hour. The nitrogen flow rate was 84 l. per hour. Thus the UF_6 concentration in the gas flow was about 22%. It was originally intended to introduce the UF_6 at a much slower rate, but the metering system (gas saturation principle) did not operate as expected.

During this time fluorine was introduced intermittently every hour for 10 minutes at the rate of 100 cc. per minute. Magnesium oxide (Westvac No. 2665) was introduced continuously at the rate of 5.64 g. per hour. The absorbing solution was circulated at 190 cc. per minute.

A solid U compound formed in the tower. After almost 11 hours of UF_6 introduction the introduction of UF_6 , F_2 and MgO was halted. Circulation was continued for 6 hours to dissolve this precipitate (assumed to be UO_2F_2). The greater part of the precipitate appeared to dissolve during this time. During the introduction of fluorine a deep red color formed in the solution, characteristic of the U peroxide. Such color was observed to fade completely overnight.

Samples for analysis were taken from the outlet end of the settling tank from time to time. The results are presented in Table 13.

Lines 1 and 2 are self-explanatory. Zero time has been taken as the time of the first introduction of MgO and process gas. The UF_6 flow was stopped after 14 hours. The UF_6 total time lags behind that for F_2 and MgO because of inlet lead plugging.

Line 3 lists the results of the U analyses. Note the sudden increase after the 6 hour circulation period and the subsequent leveling. Assuming that 5700 ppm. represents the maximum U content, and further assuming that the UF_6 flow was constant, the U analyses should have been those listed in line 4. The difference, listed in line 5, may be ascribed to slowly dissolving U compounds in the tower. Such compounds were observed. Assuming such compounds to be UO_2F_2 , four of the six mols of fluoride ion in each mol of UF_6 introduced would immediately enter the solution, while the other two mols of fluoride ion would await the solution of the UO_2F_2 . The amounts of fluoride ion thus 'liberated' by the UF_6 are listed in line 6. The concentrations of fluoride ion introduced as UF_6 are listed in line 7. These values are estimates based on the U analysis results. Line 8 lists the fluoride ion concentrations introduced

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as fluorine, and based on amounts deduced from the meters. Line 9 lists the fluoride ion which theoretically could be removed by the MgO added if it were 100% effective. Line 10 lists the estimated fluoride ion concentrations if the MgO is assumed to be 100% effective. Line 11 lists the estimated fluoride ion concentrations if the MgO were not at all effective. These estimated concentrations represent also the total fluoride ion introduced into the system. The values listed in lines 10 and 11 are based on the fluoride ion concentrations estimated from (1) the UF_6 introduced (corrected for estimated UO_2F_2 which was slow in dissolving) (2) the fluoride introduced as fluorine, and (3) the effectiveness of the MgO introduced. Lines 12 and 13 are self-explanatory.

The results in Table XIII indicate that U in accumulated concentrations up to 5700 ppm. may be introduced into the system without precipitation. The solubility of the U appears not to be affected by the MgO and MgF_2 in suspension, nor by the U peroxide formed. The fluoride content appears to have increased parallel to the amount introduced for the first 12 hours, the MgO apparently having little effect during this period.

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TABLE XIII

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1) UF_6 total time (hours)	0	7.5	10.5	14.0	14.0	14.0
2) F_2 and MgO total time (hours)	0	7.5	12 (1)	16	20	24 (2)
3) U ppm. by analysis	--	2280	3320	5690	5747	5757
4) U ppm. estimated	--	3000	4200	5690	5690	5690
5) U ppm. insoluble	--	720	880	0	0	0
6) F ppm. liberated by insol. U	--	155	190	0	0	0
7) F ppm. from U by analysis	--	1090	1590	2710	2750	2760
8) F ppm. from F_2 (35 ppm/hr.)	--	263	420	560	700	840
9) F ppm. pptd. by MgO 100% effect. (107 ppm/hr.)	--	800	1280	1710	2140	2570
10) F ppm. estimated if MgO was 100% effective	--	4987	5199	5839	5549	5259
11) F ppm. estimated if MgO was 0% effective	--	5787	6479	7549	7689	7829
12) F ppm. by analysis	4279	5727	6470	6452	6452	6512
13) pH	11.0	10.6	10.6	10.7	10.7	10.7

(1) Followed by 6 hours of circulation with no F_2 , UF_6 , or MgO introduction.

(2) At this time a sample of the insoluble from the bottom of the settling tank was centrifuged. The color of the insoluble was the characteristic grayish-white of the MgO used, indicating that no U compounds had precipitated.

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2.4 The Reduction of the Peak Fluoride Ion Concentration

When the U content reached about 5700 ppm. the UF_6 flow was stopped. Intermittent addition of fluorine was continued at the rate of 100 cc. per minute for 10 minutes every hour. The nitrogen flow was constant at 84 l/hour. Magnesium oxide addition was continued at the rate of 5.64 g. per hour. Such a rate furnishes, in one hour, three times the theoretical amount necessary to react with the amount of fluorine introduced during the same time interval. The solution was continually circulated at the rate of 190 cc. per minute.

Samples for analysis were removed as before. The results are presented in Table XIV, and the accompanying notes. Table XIV includes for convenience some results reported in Table XIII.

TABLE XIV

(1)	(2)	(3)	(4)	(5)	(6)
F_2 and MgO total time (hours)	U ppm by analysis	F ppm. estimated if MgO 100% effective	F ppm. estimated if MgO 0% effective	F ppm by analysis	pH
0	--	--	--	4279	11.0
7.5	2280	4987	5787	5727	10.6
12	3320	5199	6479	6470	10.6
16 (1)	5690	5839	7549	6452	10.7
20	5747	5549	7689	6452	10.7
24	5767	5259	7829	6512	10.7
28	5727	4967	7965	5624	10.7
33	--	4602	8135	5989	10.7
35	--	4456	8203	4533	10.7
37	--	4310	8271	4419	10.7
39	--	4164	8339	--	10.8
41	5850	4018	8407	4912	10.8
43	--	3872	8475	4839	10.9
45	--	3726	8543	3291 (?)	10.9
47	--	3580	8611	4849 (?)	10.9
49	5900	3434	8679	--	10.9
51	--	3288	8747	3872	10.9
53	--	3142	8815	3355	11.0
55 (2)	6100	2996	8883	3548	11.0
56	5735	2923	8917	3711	11.0
58	5575	2777	8985	3523	11.0
60	--	2631	9053	3000	11.0
62	--	2485	9121	2903	11.0
66	--	2173	9257	3629	--
68	5690	2027	9325	3532	11.0
70	--	1881	9393	3211	--
72	--	1735	9461	3410	11.0
74	--	1589	9529	3211	--
76 (3)	5730	1443	9597	--	--

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TABLE XIV (CONT'D)

- (1) C-616 flow stopped
Centrifuged slurry from bottom of settling tank showed only white insoluble material.
- (2) Four liters of water added to settling tank at this time.
- (3) Centrifuged slurry from bottom of settling tank showed only white insoluble material.

In table XIV, column 1 lists the total accumulated time in hours of fluorine and magnesium oxide addition starting at the time of the first introduction of C-616 into the system. Column 2 lists the U analyses. It will be noted that between 20 and 55 hours there is a steady increase in the U concentration. This due to the loss of water from the solution by evaporation. After the 4 liter dilution at 55 hours the U concentration was reduced but then continued to climb as more evaporation took place.

Column 3 lists the estimated concentration of fluoride ion if the MgO, added at the rate of 5.64 g/hr., were 100% effective in removing fluoride ion. Such maximum rate of removal should be 107 ppm/hr. Column 4 lists the estimated concentration of fluoride ion if the MgO were not effective at all. This represents the total fluoride ion added. Column 5 lists the fluoride ion concentration found by analysis. The accuracy of the estimates and analyses of columns 3, 4 and 5 do not warrant reporting to the significant figures listed. The estimates in columns 4 and 5 do not take into account the changes in total volume due to evaporation and dilution. The fluctuations noted in column 5 may be due to inaccuracies of sampling and analysis. Column 6 lists the pH values of the various samples.

When fluorine was first introduced the red color characteristic of the U-peroxy complex which was formed disappeared in a few hours as fluorine addition continued. However, the color became more permanent, until at 76 hours there was little tendency to fade after the initially partial fading of the intense color formed at the base of the tower. At this time a colorimetric analysis for U-peroxy complex indicated that about 12% of the U present was in the form of the U-peroxy complex.

After 76 hours the fluorine addition was stopped. All through the experiment MgO and MgF₂ were observed to settle quickly except for a small amount remaining suspended.

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25 General Conclusions

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The results presented in Table XIV indicate that under the conditions of the experiment:

- (1) Fluoride ion may be precipitated by MgO without interference with the complete solution of the U compounds up to concentrations of 6000 ppm; fluctuations in the U content are no more than those expected due to evaporation and dilution; failure of the appearance of any colored compounds in the insoluble is reasonably good indication that no U precipitation had taken place.
- (2) With the excess of MgO used a peak fluoride concentration of 6500 ppm. can be reduced to 3200 ppm. in about 48 hours even though fluorine addition continues; the fluoride ion concentration follows rather closely that estimated from the assumption of 100% effectiveness of the MgO until a concentration of about 3200 ppm. is reached; when this concentration is reached, continued addition of MgO decreases the concentration very little.
- (3) Changes in pH during the experiment were small, varying between 10.6 at peak fluoride ion concentration and 11.0 at the equilibrium concentration.
- (4) The settling rate of the MgO added and MgF_2 formed appears satisfactory.

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PART FOUR3. The Effect of MgO Addition Without Simultaneous
Fluorine Addition

After 76 hours the addition of fluorine was halted. The addition of magnesium oxide at the rate of 5.64 g/hour was continued, however, and the solution circulated at the former rate of 190 cc/min. During the 80 hours, which followed the U and fluoride concentrations and pH were followed.

The results are presented in Table XV and the Accompanying notes. The variations in the values of column 2 are due to evaporation dilution. The irregularities of column 3 are probably due to inaccuracies of sampling and analysis. The and is clear, however. The hours listed in column 1 included the hours recorded in Table XIV.

TABLE XV

MgO total time (hours)	U ppm. by analysis	F ppm by analysis	pH
79	--	2936	10.9 ⁸
83	5740	2831	--
84.5	--	2856	10.9 ⁸
90.5	5880	2677	11.1 ⁰
95	--	2677	11.1 ⁹
101	6090	2421	--
105	--	2447	11.2 ¹
115 (1)	6540	2421	11.2 ⁰
121	5730	2446	11.2 ⁰
129	--	2483	11.2 ⁶
138	5760	2662	--
148	--	2421	11.2 ⁹
155.5	6500	--	11.3 ¹
159.5 (2)	--	2630	--

(1) System diluted with 3 liters of water at this time.

(1) and (2)

Centrifuged slurry from bottom of settling tank showed only white insoluble material.

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24.

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The results presented in Table XV indicate that:

- (1) When MgO addition is continued at the rate of 5.64 g/hour without simultaneous addition of fluorine or process gas, the fluoride concentration in 80 hours is lowered very little below that of the so-called equilibrium value.
 - (2) The pH during the same period rises at a steady rate from 10.98 to 11.31, indicating that in plant operation excessive addition of MgO during a period of no fluorine addition should be avoided.
 - (3) The excessive MgO does not interfere with the complete solution of the U compounds present at a concentration of about 6000 ppm. of U.
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4.0 Reduction of the Rate of Magnesium Oxide Addition

After 160 hours, the intermittent addition of fluorine was resumed at the rate of 100 cc/minute for 10 minutes during each hour. The nitrogen flow was continuous at the rate of 84 liters per hour. The solution was circulated at the rate of 190 cc/minute. The rate of addition of magnesium oxide was reduced to 2.26 g/hour which is 1.2 times the theoretical amount necessary to react with the fluorine introduced during the same time interval. The fluorine introduced during the 35 hours was 35 liters, equivalent to about 1200 ppm. in the system as a whole.

These conditions continued for some 35 hours. The U and fluoride concentrations and pH were followed. The results are presented in Table XVI and accompanying notes. The hours listed in column 1 include the hours reported in Table XV. The variations in column 2 are due to evaporation and dilution as noted. The irregularities of column 3 are probably due to inaccuracies of sampling and analysis.

TABLE XVI

MgO total time (hours)	U ppm. by analysis	F ppm. by analysis	pH
164 (1)	6480	2016	11.20
169.5	5460	1758 (?)	11.18
173.5	--	2145	11.09
177.5	--	2185	11.02
185.5	--	2324	10.98
191	--	2483	10.92
196.5	--	2500	11.00
199.5	--	2522	11.00
(2)	5710	2299	--

(1) System diluted with 3 liters of water at this point.

(2) After 4 hours of circulation.

(1) and (2)

Centrifuged slurry from bottom of settling tank showed only white insoluble material.

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26.

The results presented in Table XVI indicate that a MgO feed equivalent to 1.2 times the theoretical is not quite sufficient to remove the fluorine as fast as it is introduced. During the 35 hours of operation an amount of fluorine equivalent to about 1200 ppm. was introduced. This indicates that the small excess of oxide used was almost sufficient. A 1.5 excess should be adequate.

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5.0 ACKNOWLEDGMENTS

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28.

REFERENCES

- (1) Burford III, W. B., Johns Hopkins Monthly Reports;
June - September 1943.
- (2) Report M-5155, pp. 7-10.

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CLASSIFIED APPENDICES

- APPENDIX A. Method of Equipment Design for Batch Condensation of Solids - W. I. Thompson and G. T. Cooper (The Kellogg Corporation)
- APPENDIX B. Experimental Study of Batch Condensation of Gaseous UF_6 to Solid - G. T. Cooper, H. C. Andersen and W. I. Thompson (The Kellogg Corporation)
- APPENDIX C. The Absorption of Fluorine and UF_6 by Sodium Carbonate Solutions - George G. Joris and Charles D. Compton (Princeton University)

CORRECTIONS *

VOLUME 16

(CHAPTER 7 - NOW APPENDIX A)

page 1, paragraph 1, line 2, read: "in another chapter."

line 3, read: "of the present chapter....."

page 6, under Literature Cited, change reference (1) to read:

Thompson, W. I., Chapter 6, this volume.

(CHAPTER 8 - NOW APPENDIX B)

page 17, Bibliography, reference (10), change to read: Thompson, W.I.,

Chapter 6, this volume.

reference (11), change to read: Thompson, W.I.

and Cooper, G. T., Appendix A.

* These corrections are to be made in the copies which were submitted for declassification.