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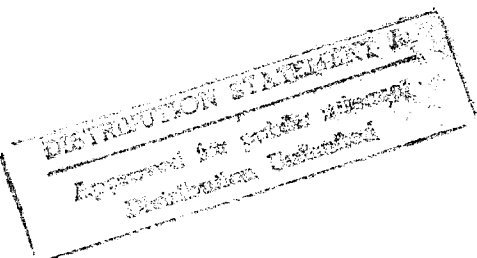
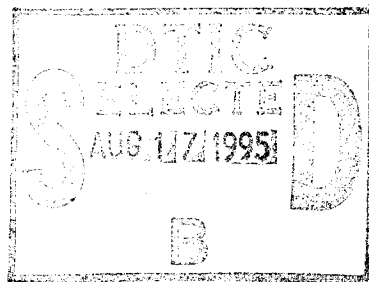
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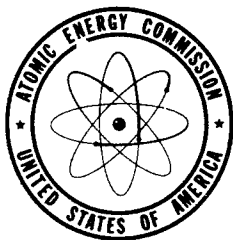
URANIUM RECOVERY FROM COMPOSITE
UF₄ REDUCTION BOMB WASTES

By
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January 28, 1954

National Lead Company of Ohio
Cincinnati, Ohio



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URANIUM RECOVERY FROM COMPOSITE UF_4 REDUCTION BOMB WASTES

1.0 ABSTRACT

A number of techniques have been investigated on a laboratory-scale for separating uranium from fluorides during the recovery of uranium from UF_4 reduction bomb wastes (C-oxide) by an HCl leach - NH_4OH precipitation process. Among these are included adsorption of fluorides from filtered leach liquors, fractional precipitation of fluorides and uranium, complexing of fluorides into forms soluble in slightly acid solutions, and fluoride volatilization from the uranium concentrate.

Solubility studies of CaF_2 and MgF_2 in aqueous hydrochloric acid at various acidities and temperatures were also conducted.

A description of the production-scale processing of C-oxide in the FMPC scrap plant has been included.

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2.0 INTRODUCTION

The processes involved in the refining of uranium metal produce certain quantities of waste materials that contain sufficient uranium values to warrant their recovery. About 85 per cent of such scrap is made up of bomb slags and liners from UF_6 reduction bombs (C-oxide). The remaining scrap consists of varying quantities of dust-collector residues, floor sweepings, sump cakes, etc.

The FMPC scrap plant was designed by Catalytic Construction Company for the purpose of handling these waste materials. This particular process was chosen on the basis of work done by the Kellogg Corporation(1). These investigators had studied a number of possible methods, including:

- (1) Mineral acid leaches in the presence of an oxidant, followed by precipitation of the uranium values using:
 - (a) ammonium hydroxide
 - (b) hydrogen peroxide
 - (c) ammonium phosphate
- (2) Alkali carbonate leaches.
- (3) Solvent extraction with TBP.
- (4) Ion exchange.

They concluded that, from both processing and economic standpoints, a hydrochloric acid leach in the presence of an oxidant, followed by ammonium hydroxide precipitation, was the most satisfactory method.

However, the experience of the Vitro Manufacturing Company, which employed a similar process for bomb wastes on a pilot-plant scale, has indicated that appreciable amounts of fluorides originating from the bomb slag contaminate the final black oxide product.

In view of this and the corrosion that might be experienced in subsequent refining steps if fluoride were above specification, an investigation was initiated at the FMPC laboratory to determine the extent of fluoride contamination in the black oxide product and techniques by which contamination might be eliminated or diminished.

3.0 LABORATORY OPERATIONS

3.1 Plant-Simulated Trials

A number of trials simulating the FMPC scrap recovery process (2) were made in the laboratory using Mallinckrodt (MCW) C-oxide as scrap feed material. This material was calcined at 1500^oF for one hour, pulverized to minus 100 mesh, and digested in 30 per cent HCl. The apparatus used for this work is shown in Figures 3.1-1 and 3.1-2. The digest liquor obtained was filtered and the residue washed with water at room temperature. The ratio of the volume of wash water to the volume of original liquor was approximately 1:5. Typical examples of the analyses of the acid-insoluble residues and filtered leach liquors obtained are shown in Table 3.1-1. It was observed that about 45 per cent of the material leached in this manner remained on the filter as the residue. Preliminary trials indicated that satisfactory uranium recovery was not obtained when the temperature of the digestion was allowed to fall below 80°C for an appreciable length of time.

Precipitation of uranium from filtered leach liquors was carried out at pH 6.2 using 28 per cent NH₄OH. This was done on a continuous basis (Fig. 3.1-3) at about 160^oF, using flows and conditions similar to those proposed for plant use. The diuranate slurry thus produced was held for a maximum of two hours at 160^oF prior to filtration. After filtering, the cake was washed with water (at the same temperature), using a wash to slurry ratio of about 1:5. The cake (Fig. 3.1-4) was then dried at 230^oF.

Conversion of the diuranate cake to black oxide was effected by calcination at 1500^oF for one hour (Fig. 3.1-5). Typical analyses of the dried diuranate cake, the diuranate filtrate, and the final uranium concentrate are given in Table 3.1-2.

From the data shown in the tables, it can be seen that the uranium concentration in the acid-insoluble residue did not exceed 0.05 per cent and the uranium concentration in the diuranate filtrate did not exceed 0.001 g/l - both of which are tolerable for discard materials. However, the fluoride concentration was found to vary.

Examination of the data obtained from the analyses of the uranium concentrate (Table 3.1-2) showed a definite correlation between the magnesium and fluoride concentrations, but none was apparent between fluoride, uranium, and calcium. This seemed to indicate that the majority of the fluoride was present as MgF_2 . The displacement of the experimental curve from the theoretical MgF_2 curve (Fig. 3.1-6) can be explained by the presence of other insoluble magnesium compounds (probably including MgO).

Fluctuations in the fluoride content of the uranium concentrate could have been a result of using a heterogeneous scrap material for these experiments. A high fluoride solubility in the leaching step would be expected if the soluble-calcium content of such liquors were small, since magnesium fluoride is considerably more soluble than calcium fluoride under these conditions.

TABLE 3.1-1

ANALYSES OF STREAMS FROM LABORATORY SCRAP RECOVERY EXPERIMENTS

Trial No.	Acid Insoluble Residue (%)			Filtered Leach Liquor (g/l)				
	<u>U</u>	<u>F</u>	<u>Ca</u> Mg	<u>U</u>	<u>F</u>	<u>Ca</u> Mg		
P-21	0.042	51.0	28.4	20.6	0.50	1.51	10.8	34.1
P-23	0.006	48.0	48.3	4.9	-	0.75	7.5	37.6
P-24	0.013	41.7	26.7	4.1	3.5	1.06	3.8	38.8
P-25	0.007	48.0	49.6	3.9	3.6	1.22	5.2	37.7
P-26	0.007	48.4	49.0	3.6	4.1	0.47	5.1	33.8
P-27	0.006	38.1	49.0	3.6	3.7	0.49	5.9	48.2
P-28	0.014	46.8	49.9	2.8	3.4	0.27	4.4	38.5
P-29	0.012	39.0	49.6	2.5	6.5	0.77	3.9	37.1
P-30	0.001	45.7	49.8	2.6	3.50	1.10	4.0	8.9

Scrap used - MCW C-oxide

TABLE 3.1-2

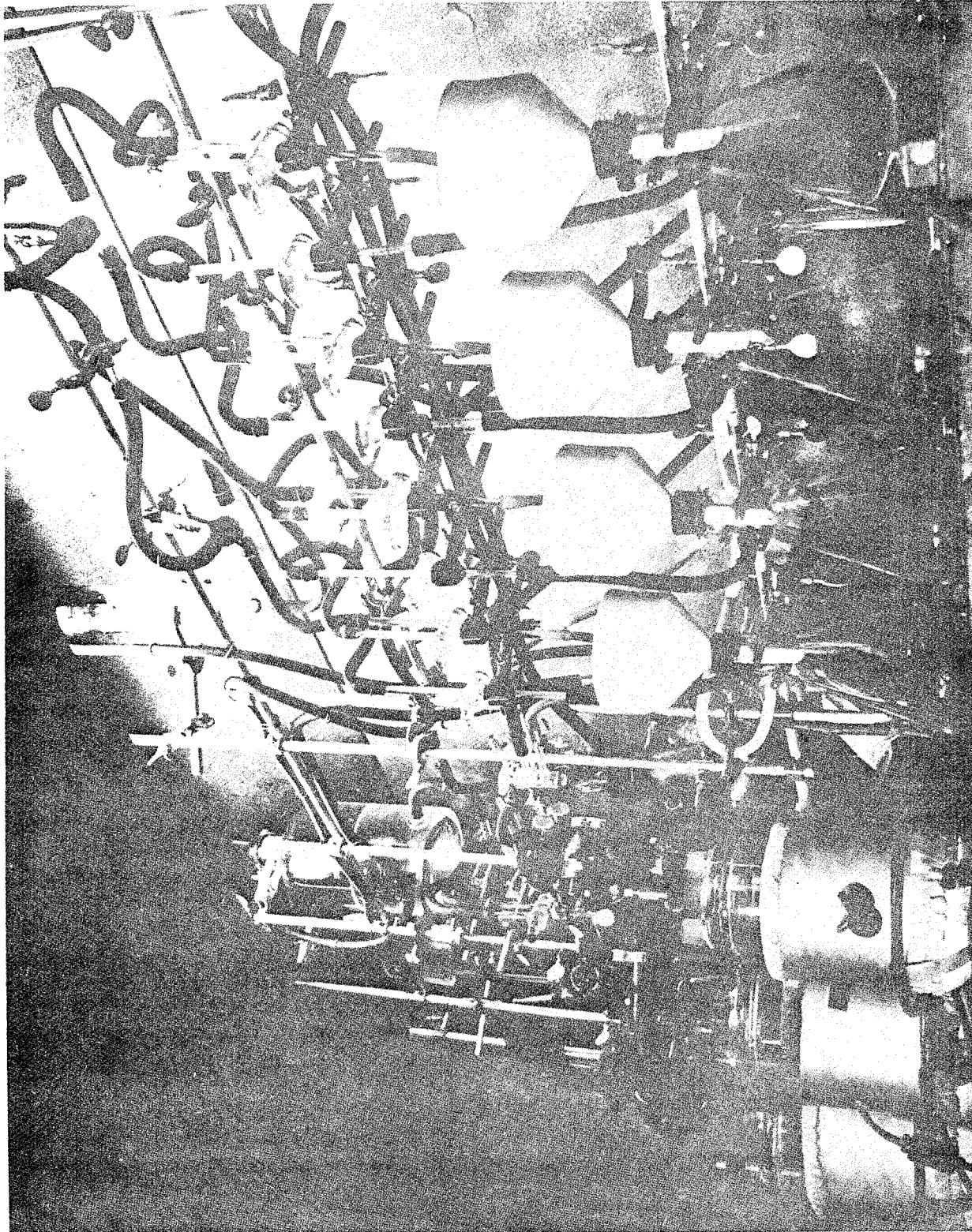
ANALYSES OF STREAMS FROM LABORATORY SCRAP RECOVERY EXPERIMENTS

Trial No.	Dried Diuranate Cake (%)		Diuranate Filtrate (g/l)			Black Oxide (%)				
	U	F	U	F	Ca	U	F	Ca		
P-21	22.6	6.80	N. Det.	0.33	8.6	25.3	37.9	13.4	1.12	18.52
P-22	-	-	-	-	-	-	32.5	13.8	1.00	16.40
P-23	62.6	0.22	-0.001	0.70	5.39	46.38	74.0	0.08	1.02	0.60
P-24	41.0	7.37	-0.001	0.34	4.92	34.59	53.3	7.05	1.84	10.52
P-25	41.0	7.44	-0.001	0.36	3.84	30.35	52.3	5.54	Sample lost	
P-26	64.0	0.14	-0.001	0.51	3.86	29.66	70.8	0.05	0.88	1.32
P-27	58.0	0.00	-0.001	0.51	3.40	29.51	67.7	-0.01	0.80	3.36
P-28	46.0	9.87	-0.001	0.39	5.27	32.59	55.0	7.28	0.74	10.9
P-29	53.0	5.25	-0.001	0.55	3.27	33.11	64.0	2.50	0.61	6.7
P-30	49.0	9.59	-0.001	0.34	4.02	30.32	-	-	-	-

Scrap used - MCW C-oxide



FIGURE 3.1-1 PRELIMINARY CALCINATION OF SCRAP MATERIAL



LABORATORY SCRAP DIGESTION AND FILTRATION UNIT

FIGURE 3-1-2

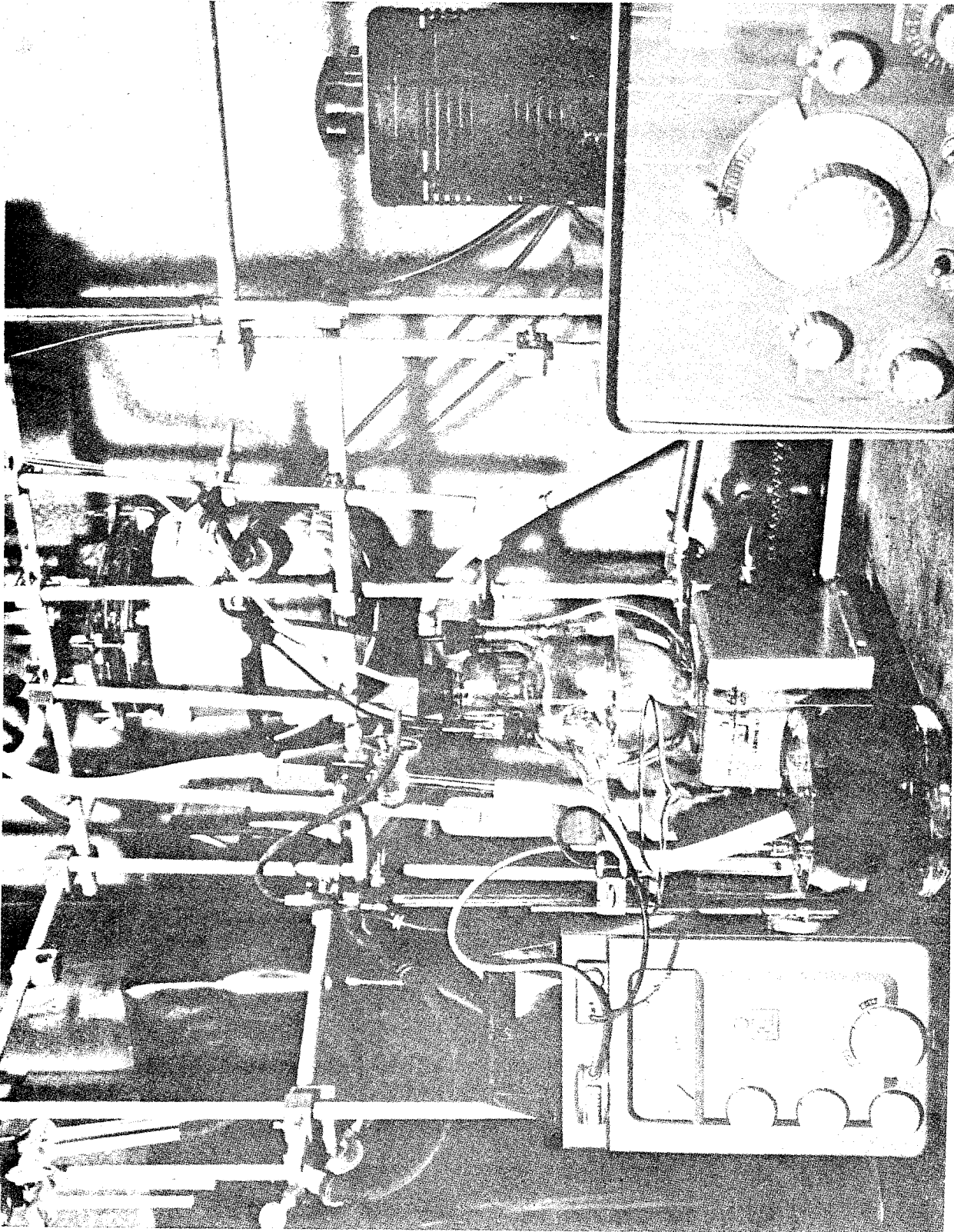


FIGURE 3.1-3 LABORATORY CONTINUOUS PRECIPITATOR

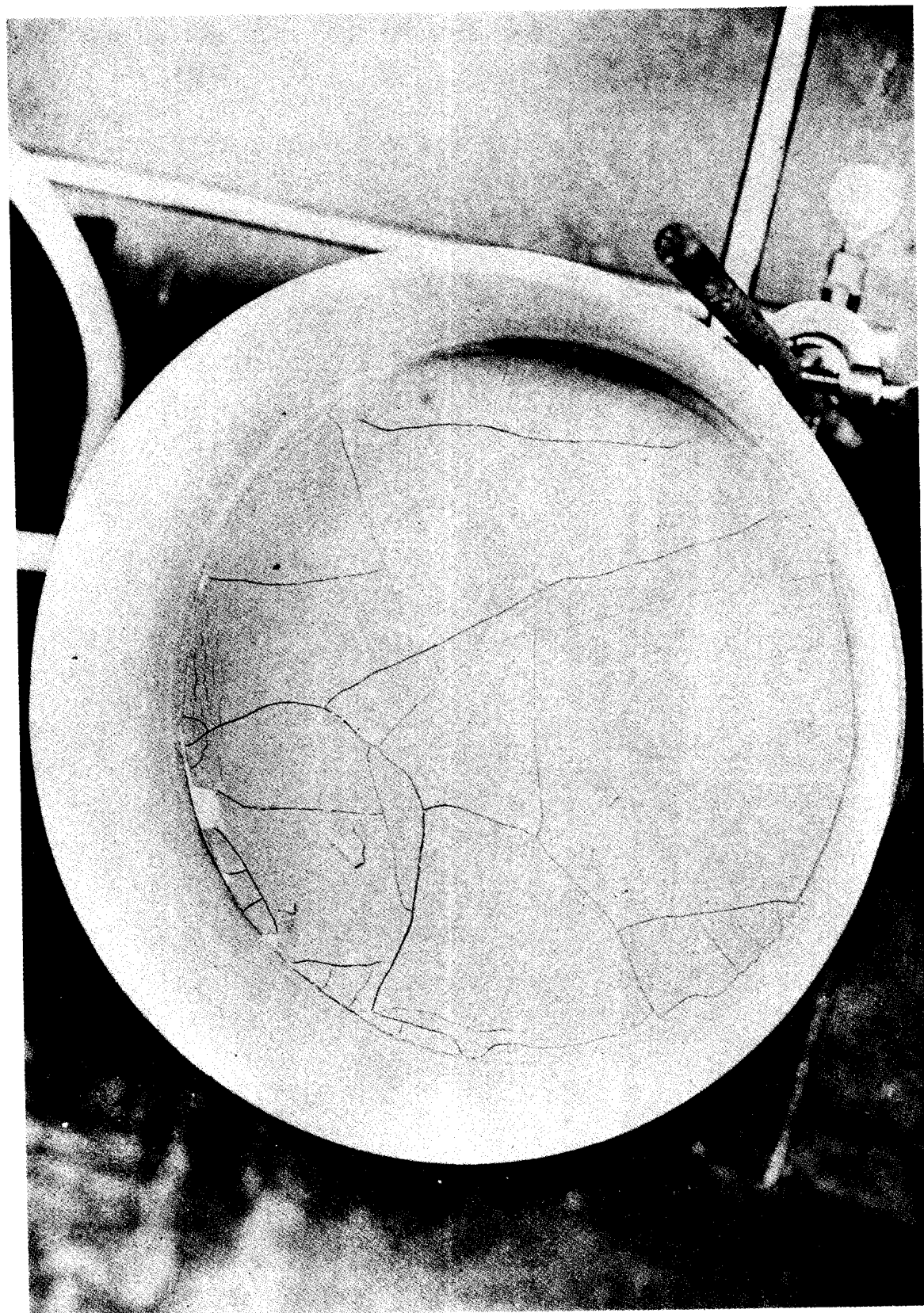


FIGURE 3.1-4 DIURANATE CAKE FROM PRECIPITATION OF C-OXIDE LEACH LIQUORS

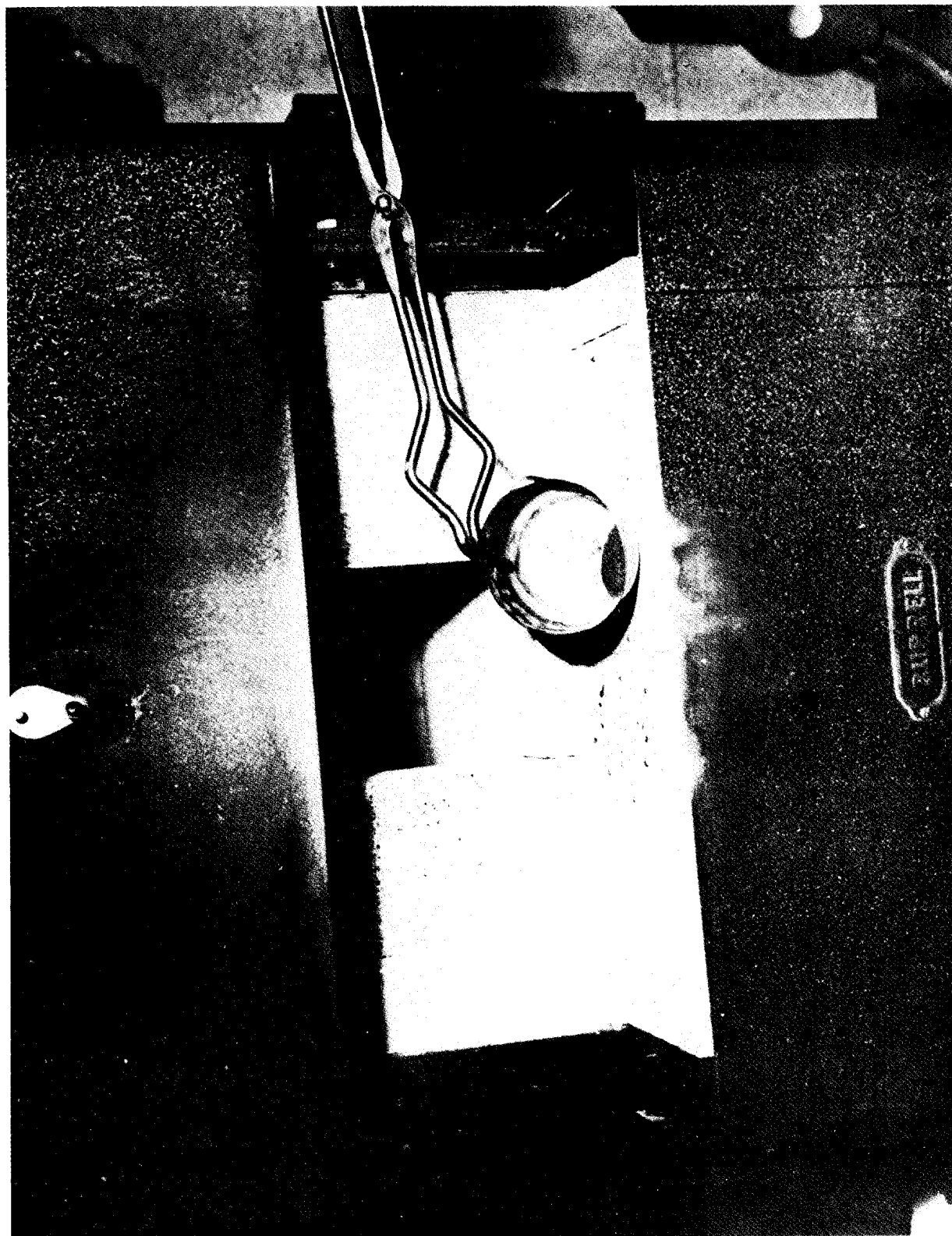
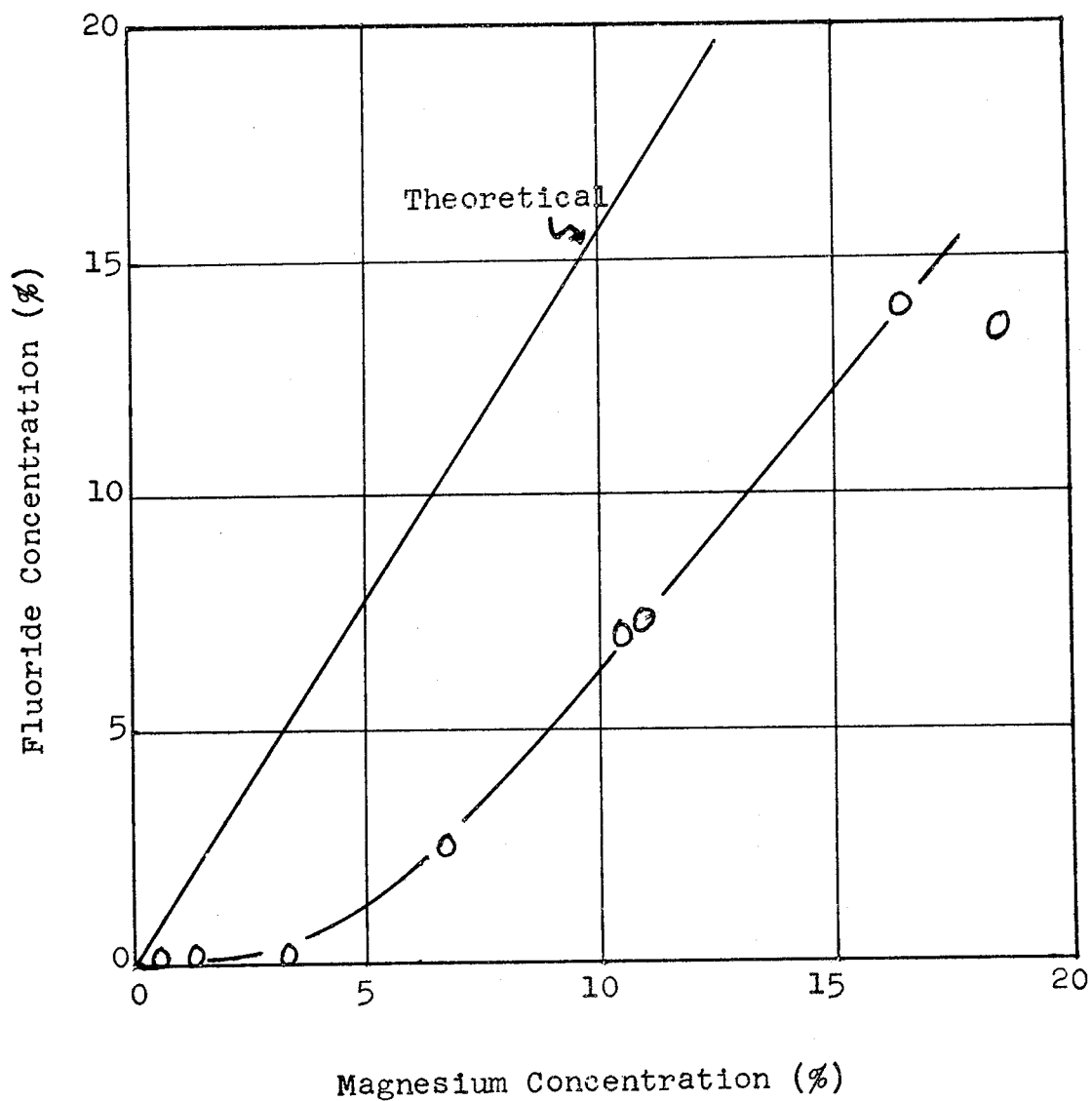


FIGURE 3.1-5 CALCINATION OF AMMONIUM DIURANATE CAKE

FLUORIDE CONCENTRATION AS A FUNCTION OF
MAGNESIUM CONTENT IN BLACK OXIDE OBTAINED
FROM PROCESSING MCW C-OXIDE FOR URANIUM



3.2 Fluoride Solubility

3.21 Solubility of CaF_2 and MgF_2 in aqueous hydrochloric acid

A series of determinations of the solubilities of commercial CaF_2 and MgF_2 in aqueous solutions of hydrochloric acid were made in the laboratory. Saturated solutions of each reagent (pH 0.5) were prepared at 25°C . The pH of these solutions was increased stepwise from pH 0.5 to 8.0 using ammonium hydroxide. At each step, the solution was allowed to stand in contact with the solid reagent for several hours prior to the determination of soluble fluorides. The results of the analyses indicated that there was a marked decrease in the solubility of CaF_2 between pH 2.0 and 3.0 and in the solubility of MgF_2 between pH 4.0 and 5.0 (Fig. 3.2-1, 3.2-2).

A study was made of the effect of temperature on the solubility of CaF_2 and MgF_2 in aqueous HCl (pH 0.5). Samples of commercial CaF_2 and MgF_2 were allowed to remain in contact with HCl for seven hours at 27°C , 42°C , 55°C , 70°C , and 90°C . The solutions were then filtered and analyzed for fluoride.

From the results of this study (Figure 3.2-3) it was found that an increase in temperature markedly increased the solubility of both calcium and magnesium fluorides. However, this effect was more pronounced on the solubility of MgF_2 than it was on CaF_2 in the range studied.

3.22 The effect of bomb waste components on MgF_2 solubility

In order to determine the mechanisms involved in the precipitation of uranium from filtered leach liquors, a series of experiments was conducted in the laboratory using synthetic leach solutions. Hydrochloric acid solutions of MgF_2 (pH 0.5), containing varying amounts of calcium and uranium were subjected to stage-wise neutralization, using 28 per cent NH_4OH , between pH 0.5 and 8.0. The solubility of the fluorides was determined at each stage. The results are shown in Table 3.2-1.

By comparing the results of trials 1 and 2, it was found that the MgF_2 slag from bomb reductions was considerably less soluble in aqueous HCl than the commercial MgF_2 (precipitated). From the results of trials 2 to 5, it appeared that the presence of calcium in the solution markedly decreased the solubility of MgF_2 in aqueous HCl. Even at pH 8.0, 0.3 to 0.4 g/l fluoride remained in the solution in the absence of Ca^{++} ions. The presence of calcium ions in solutions of fluorides derived from commercial MgF_2 appeared to cause the fluorides to precipitate at lower pH values than when no Ca^{++} was present. The presence of uranyl ions appeared to decrease the solubility of fluorides both in the presence and in the absence of Ca^{++} ions. However, this solubility disappeared when the pH of the solution was greater than pH 5.0.

3.23 Fluoride solubility in filtered C-oxide leach liquors

A series of determinations of the solubility of fluorides in filtered leach liquors was conducted at various pH's to determine the extent to which the fluorides precipitated with the uranium values during the recovery of the latter.

The pH of filtered leach liquors, having different fluoride concentrations, was increased stepwise and the fluoride solubility was observed. The liquor containing the higher fluoride concentration showed a marked decrease in fluoride solubility in the pH range 2.0 to 4.0. The lower concentration liquor showed a slight decrease in this range, but in either case, the fluoride solubility did not drop below 0.8 g/l even a pH 7.0. These results are illustrated in Figure 3.2-4.

Samples of a filtered leach liquor (1000 ml) were precipitated with 28 per cent NH_4OH at several different temperatures. The slurries obtained were filtered and the residue washed with 200 ml water. From the analyses of the

dried cake (Table 3.2-2), it appeared that higher precipitation temperatures favored the formation of a diuranate having a higher uranium but lower fluoride content. This can probably be attributed to the higher solubility of the fluorides at the higher temperatures.

TABLE 3.2-1

THE EFFECT OF THE PRESENCE OF CALCIUM AND URANYL IONS
ON THE SOLUBILITY OF MgF₂ IN AQUEOUS HCl AT 25°C

<u>Trial No.</u>	<u>MgF₂ Used</u>	<u>Calcium Conc. (g/l)</u>	<u>U Conc. (g/l)</u>	<u>pH 1</u>	<u>pH 2</u>	<u>pH 3</u>	<u>pH 4</u>	<u>pH 5</u>	<u>pH 6</u>	<u>pH 7</u>	<u>pH 8</u>
1	Slag	71	-	0.27	0.18	0.12	0.11	0.11	0.09	0.02	0.01
2	Comm.	71	-	1.36	1.28	1.24	0.32	0.07	0.05	0.05	0.04
3	Comm.	71	0.64	0.17	0.47	0.36	0.06	0.03	0.04	0.04	0.04
4	Comm.	0	1.3	2.76	2.67	2.48	2.04	0.45	0.33	0.26	0.31
5	Comm.	0	-	3.50	3.67	3.42	3.10	0.33	0.34	0.33	0.37

Note: Uranium content of the slag was negligible.

TABLE 3.2-2

THE EFFECT OF PRECIPITATION TEMPERATURE ON THE FLUORIDE
CONTENT OF DIURANATE CAKE

Trial No.	Precipitation Temp. (°C)	pH	Weight Diuranate Cake (g)	Analysis Diuranate Cake		Volume Diuranate Filtrate (ml)	Analysis of Diuranate Filtrate (g/l)			
				U(%)	F(%)		U	F	Ca	Mg
1	27	6.0	9.23	59.9	2.74	1210	0.003	0.41	18.34	23.10
2	50	6.0	8.70	61.8	0.76	1180	0.009	0.84	18.86	22.89
3	70	6.0	8.72	63.4	0.38	1200	0.002	0.89	19.13	22.91
4	25*	6.1	7.53	61.5	2.01	1200	0.004	0.23	18.04	23.10
5	70*	6.1	9.01	61.0	0.38	1140	0.04	0.97	19.91	23.71

* Gaseous ammonia used as precipitant.
Scrap used - FMPC plant pulverized C-oxide.
Analysis of leach liquor:

Uranium	4.80 g/l
Fluoride	1.06 g/l
Calcium	21.86 g/l
Magnesium	27.39 g/l

FIGURE 3.2-1

SOLUBILITY OF CALCIUM FLUORIDE IN AQUEOUS
HYDROCHLORIC ACID SOLUTIONS (25°C)

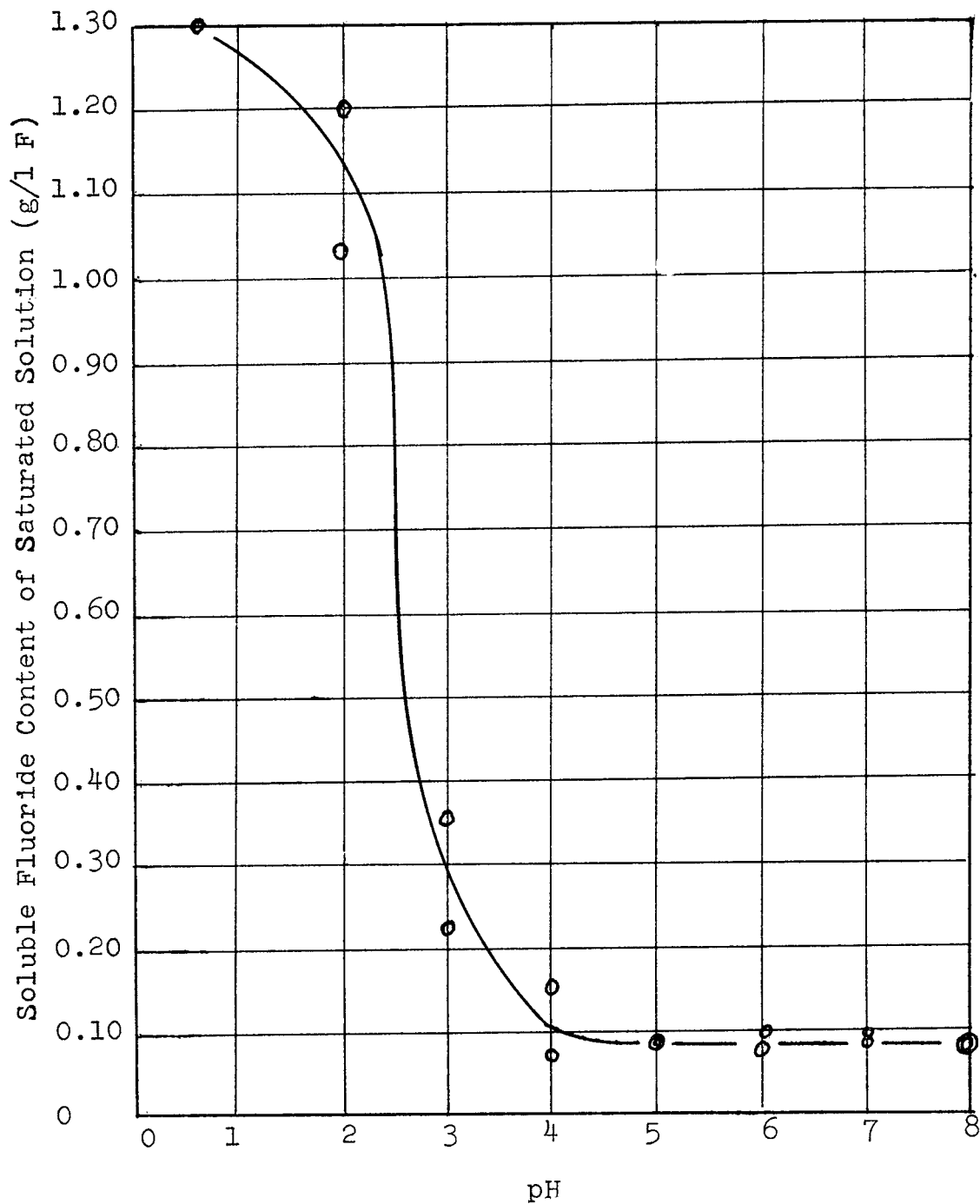


FIGURE 3.2-2

SOLUBILITY OF MAGNESIUM FLUORIDE IN AQUEOUS
HYDROCHLORIC ACID SOLUTIONS (25°C)

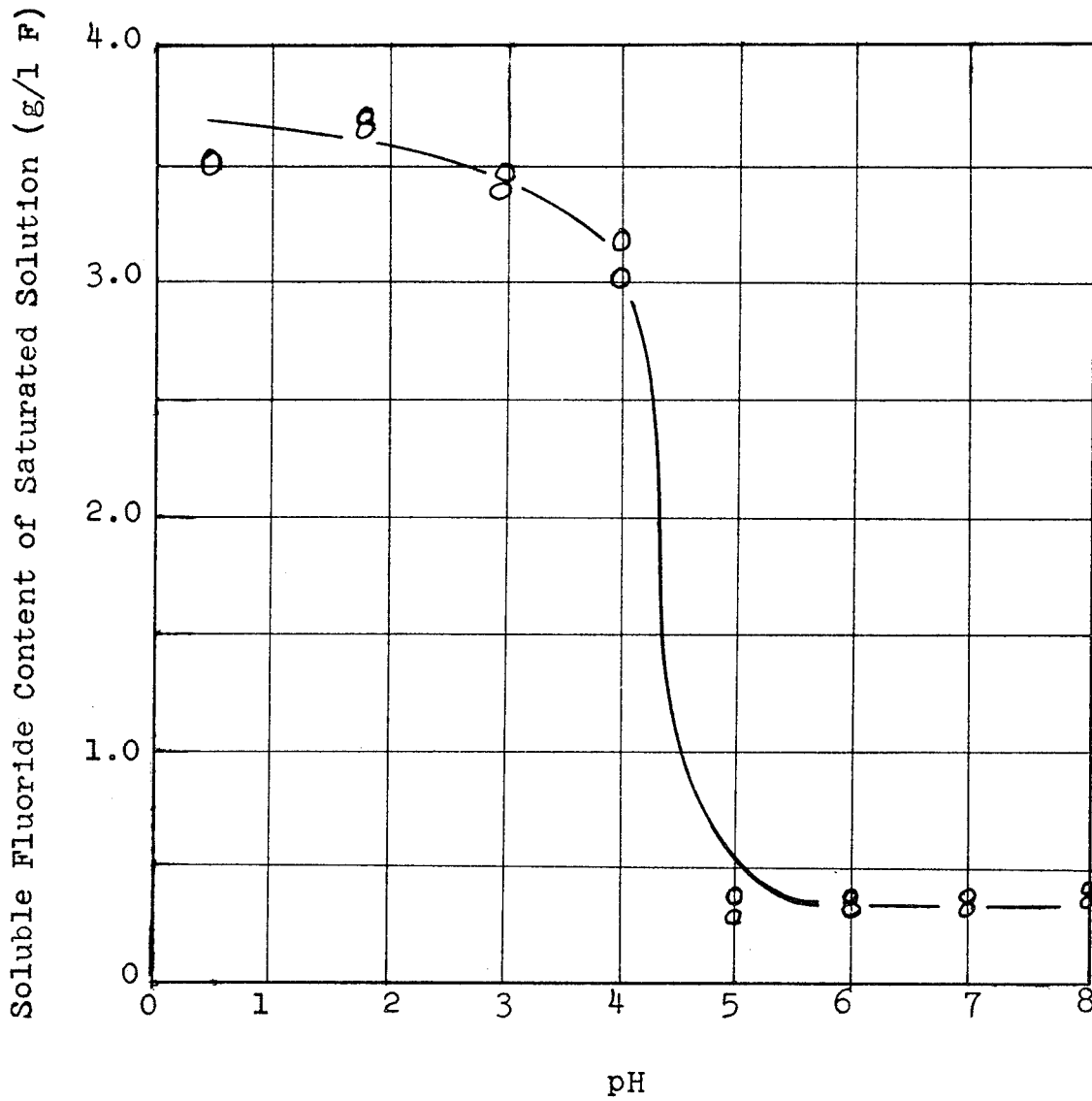


FIGURE 3.2-3

THE EFFECT OF TEMPERATURE ON THE SOLUBILITY OF
 CaF_2 AND MgF_2 IN AQUEOUS HCl (pH 0.5)

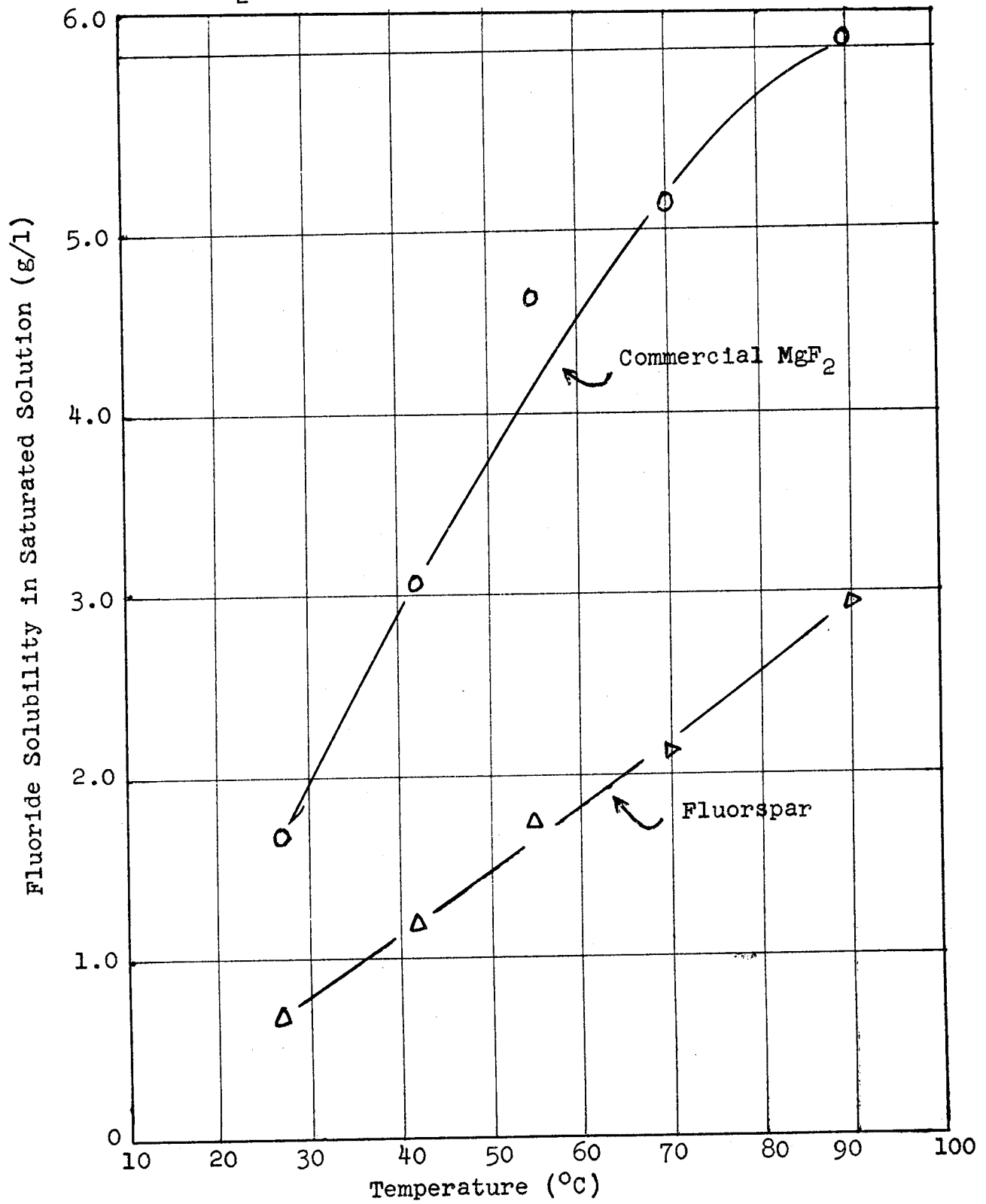
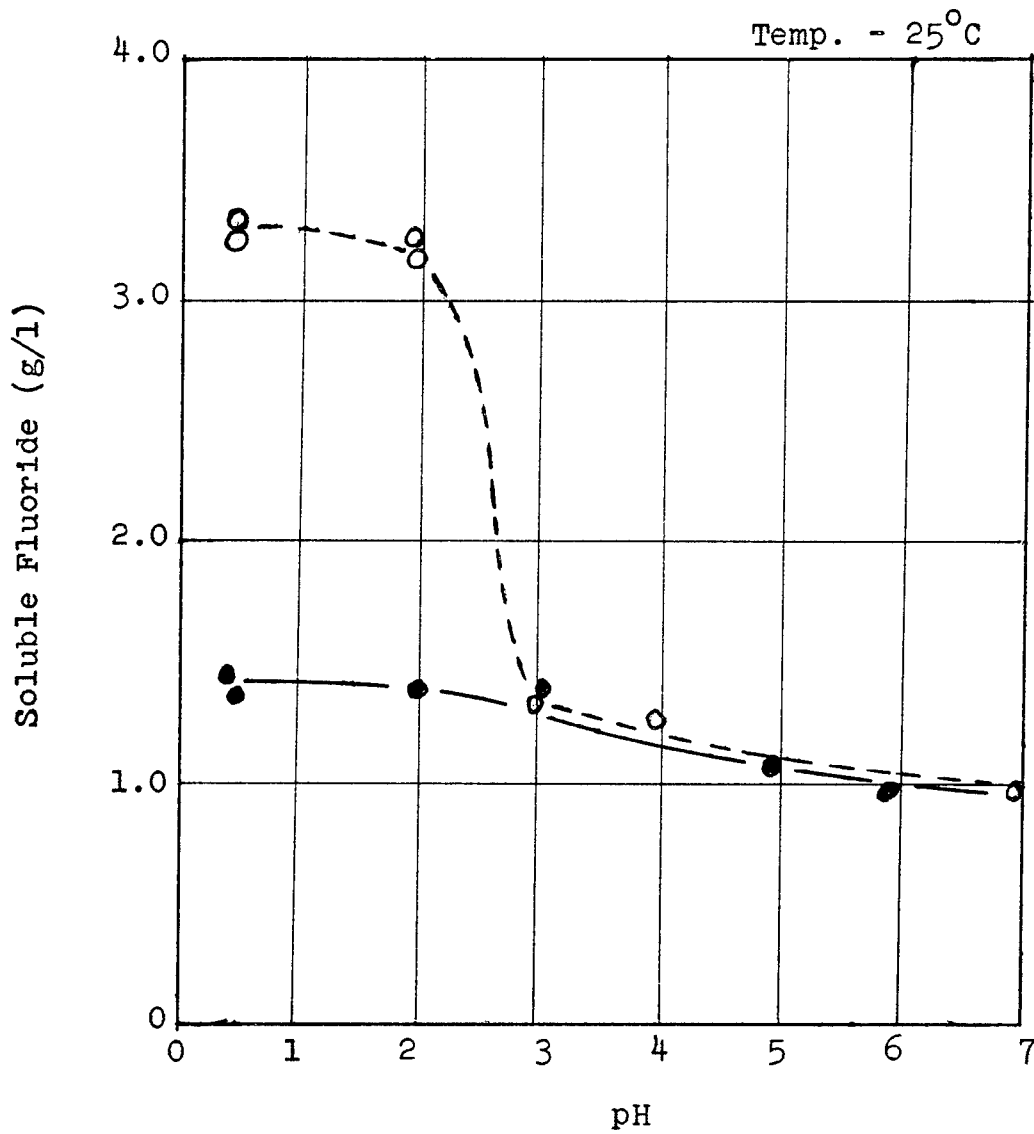


FIGURE 3.2-4

SOLUBILITY OF FLUORIDES IN FILTERED C-OXIDE-HCL
LEACH LIQUORS AT VARIOUS pH'S



3.3 Removal of Fluorides from FMPC Process Stream

3.31 Adsorption of fluorides

A number of investigators have reported that fluorides can be quantitatively removed from water using different adsorbents. A series of experiments was conducted to determine the effect of such adsorbents in removing fluorides from filtered leach liquors.

(1) Activated Alumina

Some observers (3,4,5) have shown that activated alumina beds have been successful in removing trace quantities of fluorides present in water and that the alumina thus used can be regenerated by treatment with an 8% NaOH solution.

Samples of filtered leach liquors were slurried with different quantities of activated alumina. It was found that, although the fluoride ion was removed from the solution, concurrently large quantities of uranyl ions were also removed (Fig 3.3-1).

(2) Carbon

Activated carbon was also used in an attempt to selectively adsorb fluoride ions from filtered leach liquors; however, no fluoride adsorption was detected.

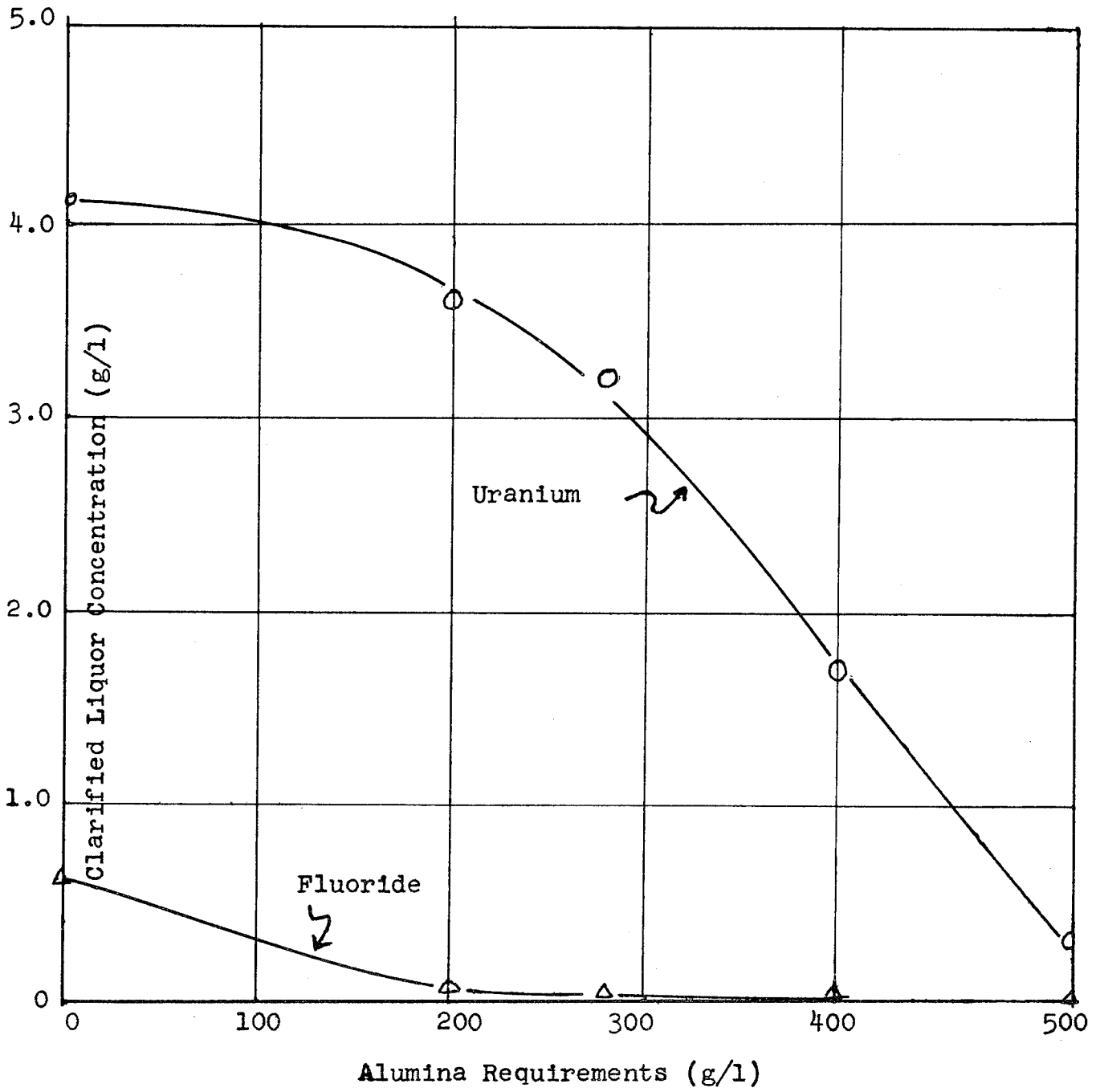
Since some investigators (6,7) had indicated that the carbon had to be pretreated with a sodium hydroxide wash followed by an HCl rinse, additional adsorption trials were made using the treated material with filtered C-oxide leach liquors. Essentially no fluoride adsorption was observed.

(3) Silica Gel

Allowing filtered leach liquors to pass slowly through a bed of silica gel also failed to show a reduction in the fluoride content of the treated liquor.

FIGURE 3.3-1

ADSORPTION OF FLUORIDES AND URANIUM FROM CLARIFIED
HCl-MCW C-OXIDE DIGEST LIQUORS BY ACTIVATED ALUMINA



3.32 Fractional precipitation

Several attempts were made in the laboratory to separate uranium and fluorides by fractional precipitation. Samples of filtered leach liquors were fractionally precipitated at pH 3.5 to 4.5, and then at pH 6.2. It was found that a dried diuranate cake containing less than 0.5 per cent fluoride could be obtained by this procedure (Table 3.3-1). Appreciable quantities of uranium were precipitated with the fluoride during the first fractionation. These would have to be recovered by recycling the first precipitate fraction to the leaching step.

3.33 Complexing of fluorides

The duPont Company (8) has claimed to be successful in eliminating fluoride contamination from peruranic acid during the precipitation of the latter from sulfuric acid leach liquors. Their procedure involved the addition of aluminum ions for the purpose of complexing the fluorides.

An attempt was made in the laboratory to effect similar results during the precipitation of uranium from hydrochloric acid leach liquors by ammonium hydroxide.

The work of Finkelstein and Achterberg (9) had shown that the soluble $\text{AlCl}_3 \cdot \text{AlF}_3$ was formed when aqueous solutions of aluminum chloride were heated with solid CaF_2 in acid solution. Although the fluorides present in the filtered leach liquors were in solution, it was thought there was a possibility that a similar reaction would take place. However, M. H. Merchant (10) indicated that the fluorides would precipitate from solution as alkaline earth fluorides or as fluoaluminate complexes in the presence of aluminum chloride around pH 4.0.

In order to determine the effect of aluminum chloride on the solubility of fluorides in a solution of MgF_2 in HCl, the solution was treated with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and the pH increased stepwise, using 28 per cent ammonium hydroxide. It was found that essentially all of the fluoride had precipitated at pH 4.3 but that the magnesium did not separate until pH 5.4 (Table 3.3-2).

The residue obtained from filtering the liquor at pH 4.3 was found to contain 24.2% fluoride but only 2.55% magnesium. This was in marked contrast with the results obtained from precipitating pure MgF_2 solutions (Section 3.21), where the two ions separated in the stoichiometric ratio. This would seem to indicate that the fluoride was separating largely as the complex aluminum compound, as was indicated by Merchant's article.

The addition of aluminum chloride or boric acid to filtered scrap-leach liquors also failed to appreciably increase the fluoride solubility in the pH range 0.5 to 6.0.

TABLE 3.3-1
FRACTIONAL PRECIPITATION OF C-OXIDE LEACH LIQUORS

Trial No.	First Fraction		Temp. (°C)	% U in Cake	Temp. (°C)	Second Fraction		% U in Cake
	Temp. (°C)	Wt. Cake (g)				pH	% F in Cake	
1	28	3.6	0.95	36.1	70	6.2	1.29	72.2
2	29	4.1	0.99	36.1	70	6.2	0.00	75.3
3	29	4.5	2.70	52.6	70	6.2	0.15	71.7
4	70	3.5	0.66	17.8	70	6.2	0.05	69.7
5	70	4.0	1.73	45.9	70	6.2	0.14	73.0
6	70	4.5	4.14	57.2	70	6.2	0.47	57.0

Volume Leach liquor - 1000 ml
Scrap used - FMPC Plant Pulverized
Approximate Leach Liquor Analysis:

Uranium - 4.5 g/l
Fluoride - 1.0 g/l

TABLE 3.3-2

THE EFFECT OF ALUMINUM CHLORIDE ON THE SOLUBILITY
OF FLUORIDE AND MAGNESIUM
IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS OF MgF_2

Trial No.	pH	Reaction Time	Analysis of Solubles(g/l)	
			F	Mg
Orig. Solution	0.5	24 hr	1.60	1.54
1	4.3	24 hr	0.06	1.07
2	5.4	20 min	0.06	0.05
3	6.4	20 min	0.04	0.86
Residue from Trial 1			24.2	2.55

Wt. of $AlCl_3 \cdot 6H_2O$ added - 6.6 g/l of solution.
Temperature - 90°C.

3.34 Fluoride volatilization from diuranate cake

Several techniques of volatilizing the fluorides present in the ammonium diuranate cake were investigated as possible methods of producing a low-fluoride uranium concentrate.

(1) Calcination

A study was made of the effect of both the time and temperature of calcination on the volatilization of fluorides from diuranate cake. Samples of the cake, which had been produced in the laboratory using MCW C-oxide, were exposed to temperatures from 500° to 1500°F for one hour, and the fluoride concentrations of the resulting residues were determined. It was found that temperatures in excess of 1250°F were necessary to effect a substantial reduction in the fluoride content of the black oxide formed (Fig. 3.3-2).

Calcination of diuranate cakes for prolonged periods was also found to be beneficial in removing fluorides (Fig. 3.3-3).

(2) Particle Size Studies

In a series of experiments, samples of moist diuranate cake were dried, pulverized, and sieved. The various sieve fractions as well as some of the moist cake were then subjected to calcination for one hour at 1500°F. Results of fluoride analyses on the products obtained from this treatment indicated that fluoride volatility was not substantially greater for the finer particles than for the more coarse ones. The moist material showed a considerably greater fluoride loss than the screened fractions - probably from pyrohydrolysis due to the water present. The results are summarized in Table 3.3-3.

TABLE 3.3-3

THE EFFECT OF PARTICLE SIZE OF DIURANATE CAKE
ON VOLATILIZATION OF FLUORIDES

<u>Sieve Fraction</u>	<u>Per Cent Fluoride in Product</u>	
	<u>Trial 1</u>	<u>Trial 2</u>
✓ 20	12.5	11.0
- 20 ✓ 60	11.3	11.0
- 60 ✓ 100	10.6	10.9
- 100 ✓ 200	12.1	10.3
- 200 ✓ 325	11.4	9.7
- 325	10.5	8.4
Wet Cake	9.1	-

Calcination Temp. - 1500° F.

Calcination Time - 1 hr.

(3) Pyrohydrolysis

A study was conducted to determine the efficiency of pyrohydrolysis on the removal of fluorides from plant-produced black oxide and diuranate cake. The results of the study indicated that temperatures around 1800°F were required for satisfactory volatilization of fluorides in black oxide, while 1500°F sufficed for processing the diuranate cake. Prolonged heating periods were found to be beneficial (Fig. 3.3-4 and 3.3-5).

The black oxide was observed to be less reactive with steam than was the diuranate cake.

(4) Sulfuric Acid Roast

Samples of plant-produced diuranate cake were calcined in the presence of varying quantities of sulfuric acid at different temperatures. It was found that the temperature of calcination was not as critical as was the amount of sulfuric acid present. Twice the theoretical requirement of H_2SO_4 (based on the metathesis of metal fluorides and H_2SO_4) reduced the fluoride content of the cake from 4.56 to 0.05 per cent in one hour at 1500°F. Results are summarized in Table 3.3-4.

TABLE 3.3-4

SULFURIC ACID ROAST OF SCRAP PLANT DIURANATE CAKE

<u>Trial (1) No.</u>	<u>Times Theoretical H₂SO₄</u>	<u>Temperature (°F)</u>	<u>F Conc. (%)</u>
Original cake	-----	-----	4.56
1	1	1500	2.03
2	2	1500	0.05
3	3	1500	0.05
4	1	1000	4.89
5	2	1000	0.99
6	3	1000	0.10
7	1	500	3.11
8	2	500	0.19
9	3	500	0.06

(1) All samples were calcined for one hour.

FIGURE 3.3-2

FLUORIDE CONTENT OF BLACK OXIDE PRODUCT FROM SCRAP PROCESSING AS A FUNCTION OF CALCINATION TEMPERATURE

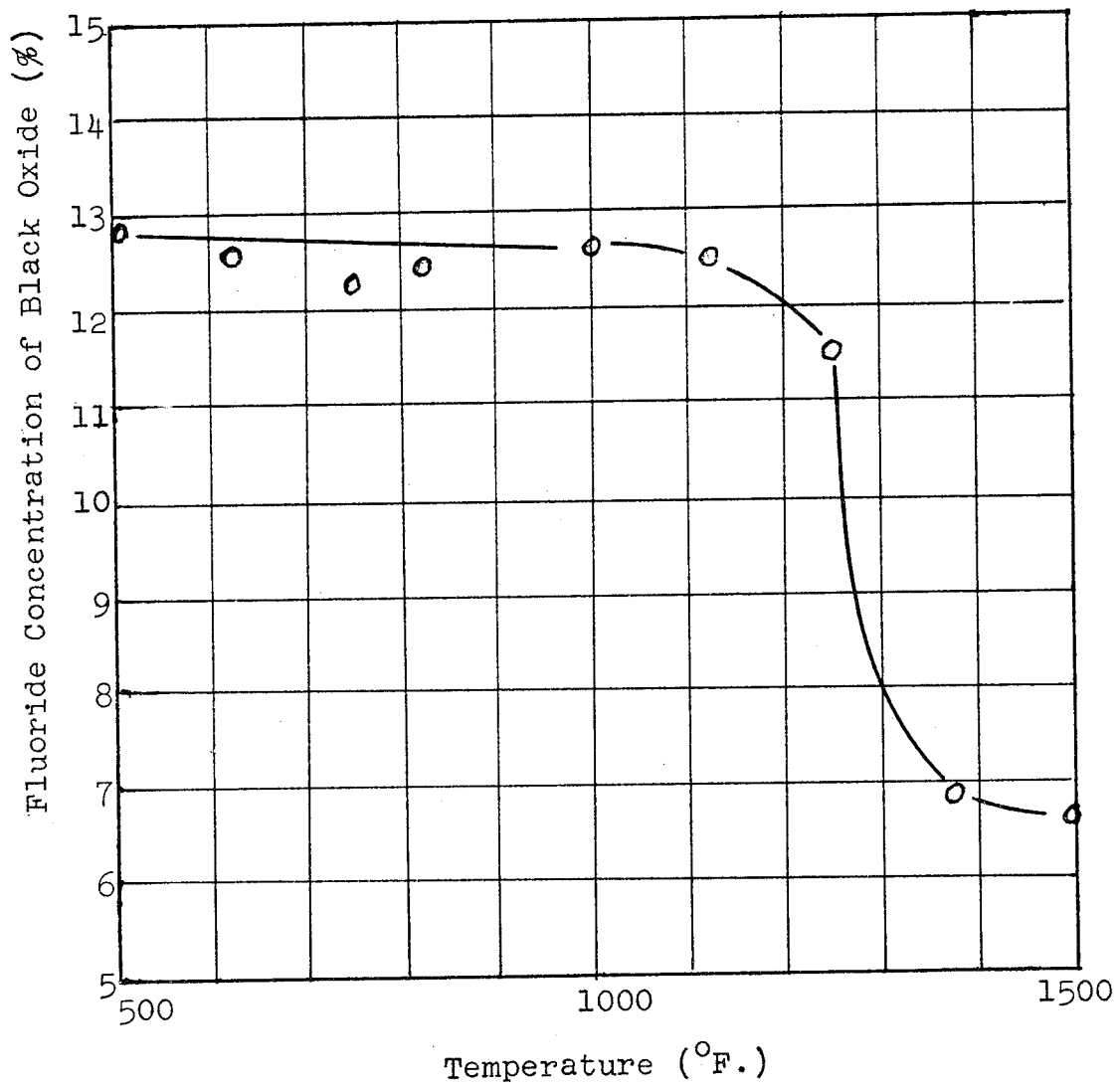


FIGURE 3.3-3

EFFECT OF CALCINATION TIME ON THE FLUORIDE CONTENT OF BLACK OXIDE FROM SCRAP PROCESSING

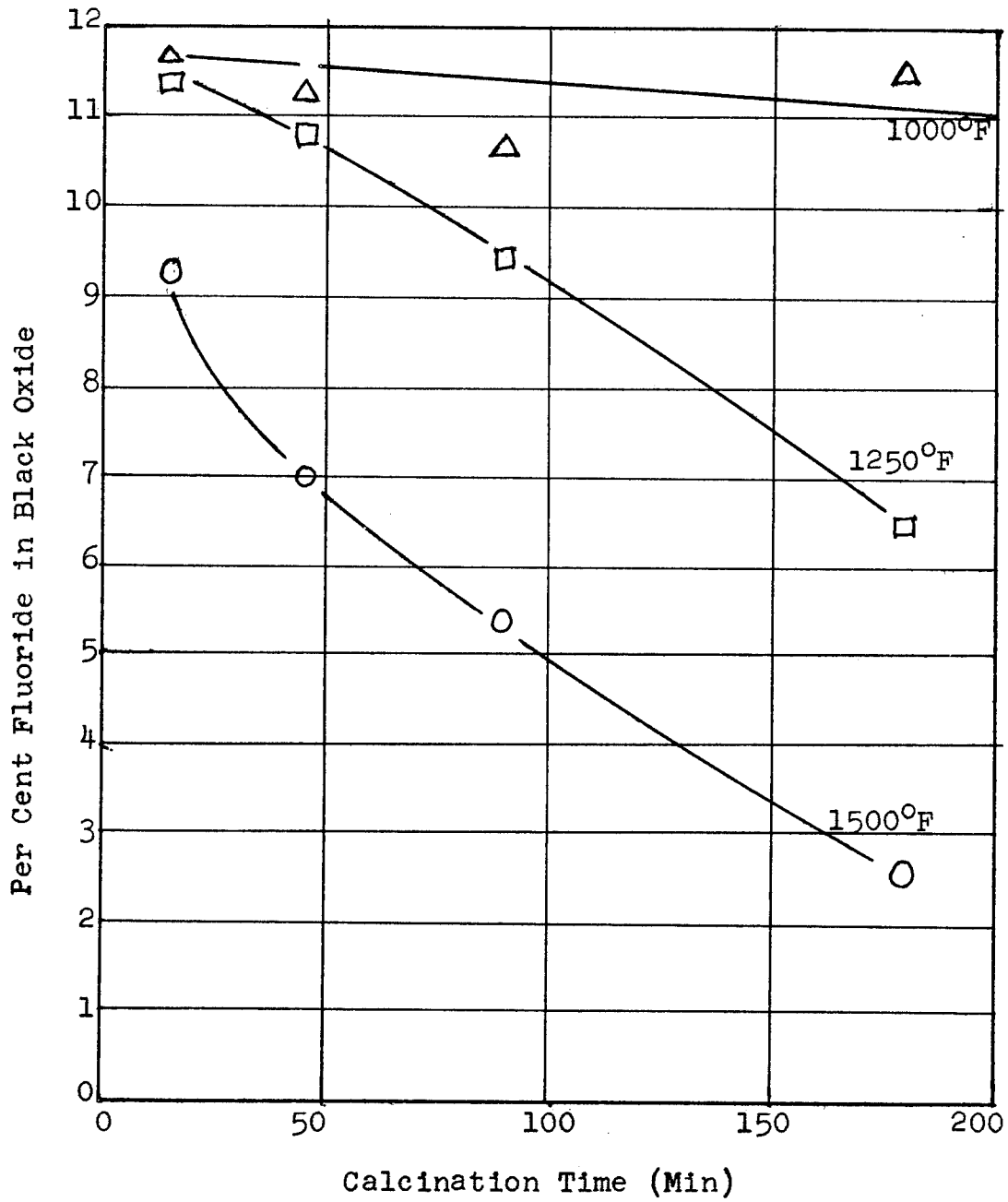


FIGURE 3.3-4

EFFECT OF TIME AND TEMPERATURE ON THE
PYROHYDROLYSIS OF SCRAP PLANT
DIURANATE CAKE

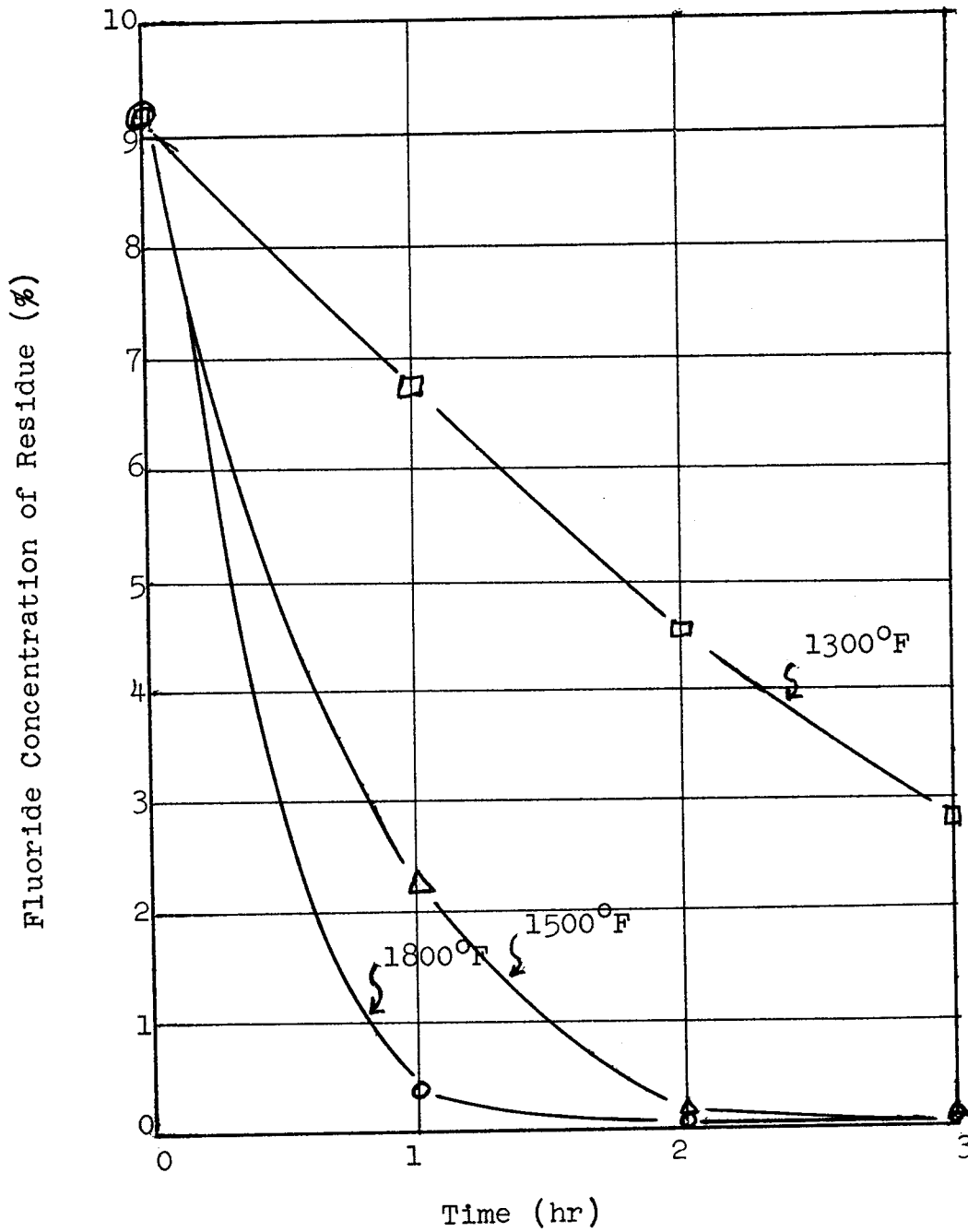
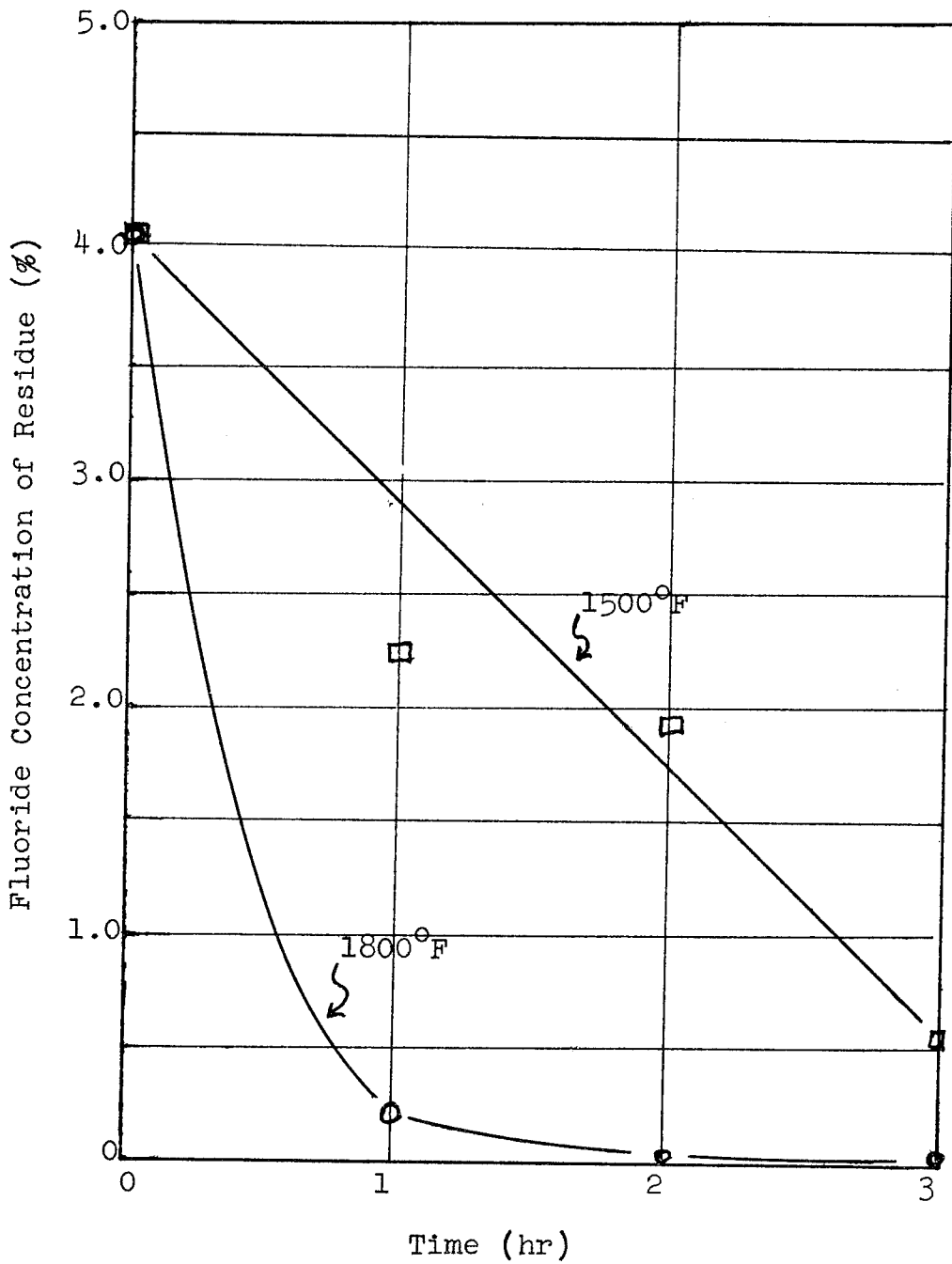


FIGURE 3.3-5

EFFECT OF TIME AND TEMPERATURE ON THE
PYROHYDROLYSIS OF SCRAP PLANT
BLACK OXIDE



4.0 PLANT OPERATIONS

4.1 Digestion

Digestion of the roasted and pulverized C-oxide proceeded very slowly due to the large amount of heat given off during the neutralization of lime present. However, it was found that the temperature of the slurry in the plant's 5000-gal tanks could be maintained at 200°F by concurrent addition of water and acid rather than by adding the 30 per cent acid alone. This reduced the time required for acid addition from about 24 hours to less than 2 hours.

A study was made on the digest liquors in the plant to determine the length of leaching period required to reduce the acid-insoluble residue to below 0.05 per cent uranium. After acid and oxidant (NaClO_3) addition was complete, hourly slurry samples were withdrawn from the digester and filtered. The residue obtained was carefully washed, dried, and analyzed for uranium (fluorometrically). The amount of fluoride solubilized was determined by analysis of the acid filtrate. From the results (Table 4.1-1) it can be seen that while extended digestion periods did not cause an increased dissolution of the fluorides present, it was beneficial in removing small uranium concentrations from the acid-insoluble residue. Between two and three hours was found to be sufficient for obtaining a residue having a uranium concentration of less than 0.05 per cent.

TABLE 4.1-1

LEACHING PERIOD - TIME STUDY

<u>Sample*</u>	<u>Digest Time (hr)</u>	<u>Final pH</u>	<u>Fluoride in Acid Filtrate (g/l)</u>	<u>% U in Acid-Insoluble Residue</u>	<u>Remarks</u>
D-137-1	0	0.8	-	0.39	
D-137-2	1	0.8	-	0.10	
D-137-3	2	0.8	-	0.030	
D-137-4	12	0.8	-	0.024	
D-140-1	1	0.9	-	0.075	
D-140-2	2	0.9		0.031	
D-140-3	4	0.9		0.018	
D-140-4	5	0.9		0.017	
D-176-1	1	0.2	1.74	0.023	
D-176-2	3	0.2	1.59	0.020	
D-176-3	4	0.2	1.50	0.011	
D-176-4	5	0.2	1.51	0.022	
D-176-4A	5	0.2	1.49	-	Acid filtrate cooled and re-filtered.
D-180-1	1	0.2	0.56	0.54	Filtration very difficult due to large amounts of finely divided carbon.
D-180-2	2	0.2	0.88	0.20	
D-180-3	3	0.2	0.97	0.20	
D-180-4	4	0.2	0.89	0.17	
D-180-5	5	0.2	0.89	0.15	

* Indicates plant batch number.
Digest time measured from final acid addition.

4.2 Precipitation of Leach Liquors

Considerable difficulty was experienced in pH control during the continuous precipitation of filtered leach liquors. Because of the small size of the precipitator (260 gal), small additions of the 28% NH_4OH caused the pH to surge considerably above 6.2. It had been shown in the laboratory that high pH values caused the coprecipitation of alkaline earth hydroxides as well as additional quantities of fluorides.

In resolving this trouble, care was exercised to maintain the pH in the precipitator slightly below 6.0. Any uranium which would fail to precipitate due to a low pH in the precipitator would separate in the diuranate slurry hold tank, where a continuous pH adjustment was maintained at pH 6.2. This hold tank was not subject to similar pH fluctuation due to its greater volume.

The use of dilute ammonium hydroxide (15%) reduced the pH fluctuations in the precipitator appreciably, thereby allowing a more careful pH control.

The holdup time of the diuranate slurry prior to its filtration was held to a minimum to prevent possible postprecipitation of fluorides.

Since the leach liquors were filtered while they were relatively hot (140°F), care was taken to maintain this temperature throughout the precipitation and diuranate filtration steps to prevent fluorides from separating on cooling. This was accomplished by steam-sparging the acid filtrate prior to precipitation.

4.3 Filtration

4.31 Acid leach liquors

An Eimco rotary vacuum filter was used for filtration of the acid leach liquors. Difficulty was experienced with agitator arms breaking due to an accumulation of solids in the basin of the filter. By cracking the valve in the basin of the filter to provide a recycle to the slurry hold tank, it was

found that longer operating periods between basin clean-outs could be obtained.

The leach slurries from thirteen different plant digest batches were examined in the laboratory with respect to their density, per cent solids, density of the clarified liquors, and settling rates of solids. This information was determined so that an agitator could be designed for keeping the solids suspended in the filter basin during filtration. The results are shown in Table 4.3-1 and Figure 4.3-1. From the data, it can be seen that the solids settled very rapidly, more than 50 per cent separating in ten minutes.

Difficulty was also experienced in pre-coating the Eimco filters by dry eduction. The particles of Filter Aid were not wetted sufficiently to form a uniformly adhering precoat. Satisfactory precoating of the Eimco filter has been accomplished by slurring a 2 per cent precoat suspension in the basin of the filter.

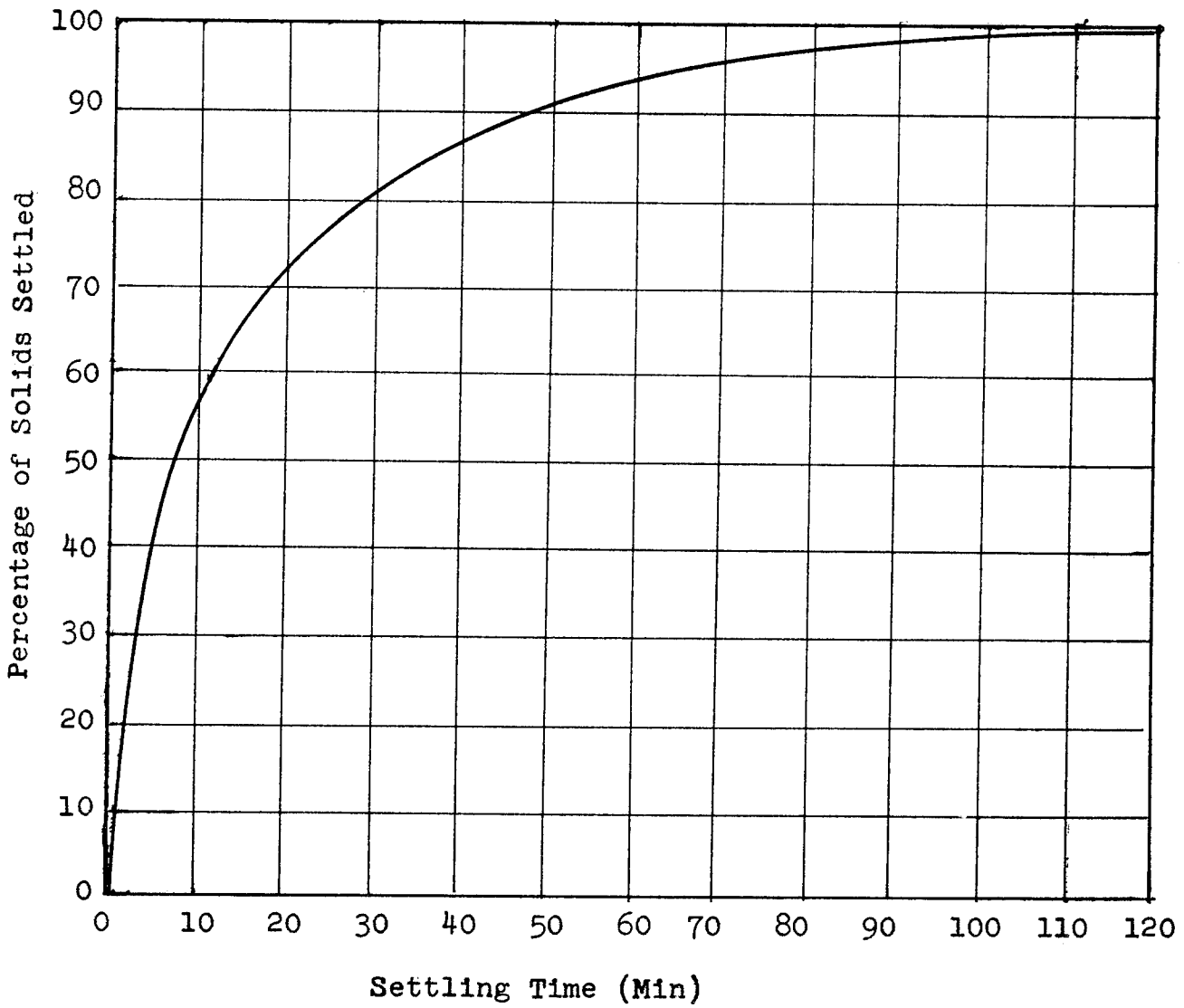
Orlon cloth was found to be more suitable than saran as a filter cloth.

TABLE 4.3-1SLURRY CHARACTERISTICS OF C-OXIDE LEACH LIQUORS

<u>Property</u>	<u>Range</u>	<u>Average</u>
Density of Slurry, g/ml	1.16-1.23	1.20
Per Cent Solids in Slurry	4.1 - 10.0	6.2
Density of Filtrate, g/ml	1.12-1.17	1.14

FIGURE 4.3-1

SETTLING RATES OF SOLIDS IN FMPC SCRAP
PLANT LEACH LIQUORS



4.32 Diuranate slurry

Satisfactory filtration of the diuranate slurry has been obtained using an Oliver rotary vacuum filter. The only difficulty to date has been the selection of a suitable precoat. It was found that coarser grades became impregnated with diuranate cake, and after the precoat had been reduced to 3/4-inch thickness the precoat had to be removed with a hammer. A number of filter cloths were torn in removing this hard mass - in addition, valves plugged and pumps stalled.

Solka Flocc (BW-100), an alpha cellulose material, was found to precoat evenly and with a minimum of cracks and fissures. This material, having a very low ash content, was found to be especially desirable in that no siliceous material was cut off the drum along with the cake. The uranium assays of the product obtained from firing the diuranate cake containing the Solka Flocc averaged 10 per cent higher than did corresponding cakes containing the siliceous filter aids.

4.4 Calcination of Diuranate Cake

Calcination of the diuranate cake is accomplished in a multiple-hearth furnace. The difficulty of charging the wet gelatinous cake into the furnace was solved by the installation of a Moyno pump, which extrudes the material onto the top hearth. The second, third, and fourth hearths are maintained at 1450°F, 1550°F and 1750°F, respectively. In the plant, as in the laboratory, it has been shown that the residence time within this furnace is important in the volatilization of the fluorides present in the material.

Pyrohydrolysis of diuranate cake has been attempted in this furnace, but has not been successful. Since the furnace is directly fired by gas burners, the necessary steam excess tended to extinguish the burners.

5.0 CONCLUSIONS

Fluoride contamination occurs in the uranium concentrate, obtained from processing C-oxide, because of the dissolution of small amounts of MgF_2 slag during leaching with HCl. These dissolved fluorides coprecipitate with the dissolved uranium during the recovery of the latter. The presence of calcium in the scrap decreases the solubility of the fluoride during leaching, but sufficient quantities of fluorides solubilize to produce an undesirable contamination of the final uranium concentrate.

Efforts to remove the fluorides from the uranium stream by adsorption from acid leach liquors have failed. Attempts to complex this ion in such a manner that it would not coprecipitate with uranium have also been unsuccessful.

Satisfactory uranium concentrates have been produced by fractional precipitation of acid leach liquors at pH 3.5 to 4.5 and then at pH 6.2. Complete uranium recovery was assured by recycling the residue from the first fraction to the leaching operation.

Calcination of the diuranate cake at temperatures above $1250^{\circ}F$ caused appreciable volatilization of the fluorides present in the cake. Fluoride volatility was enhanced by calcining the cake while moist. Pyrohydrolyzing the diuranate cake for several hours at $1500^{\circ}F$ resulted in essentially complete volatilization of the fluorides which contaminated the product.

Roasting high-fluoride diuranate cake in the presence of small quantities of sulfuric acid at 500° to $1500^{\circ}F$ has been found to be a successful method of volatilizing fluorides present. Metal sulfates remain in the product.

Through the processing of C-oxide on a production scale at FMPC, it has been found that a uranium product averaging less than 0.5% F can be produced consistently by subjecting the moist diuranate cake to temperatures of from 1400° to $1600^{\circ}F$ for approximately two hours. Careful control of pH and temperature throughout the scrap system was essential in producing a low-fluoride high-uranium concentrate.

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