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MANGANESE DIOXIDE AS A FILTER AID IN THE "25" PROCESS

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MANGANESE DIOXIDE AS A FILTER AID IN THE "25" PROCESS

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1.0 Abstract

This report presents an evaluation of manganese dioxide as a filter aid for clarifying 25 process metal solutions (solution of uranium-aluminum fuel rods in nitric acid).

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2.0 Introduction

During the semi-works scale investigations of U-235 recovery by solvent extraction in continuous counter-current columns, the packing often plugged because of insoluble material remaining in suspension in the feed solutions. At the start-up of the Pilot Plant U-235 operations, solutions were filtered with a porous stainless steel filter plate (10 micron pore size) without the use of a filter aid. This procedure was effective, but the pressure drop across the filter increased more rapidly than was desired. It appeared advisable to study the use of a filter aid from which the uranium hold-up could be easily recovered. Manganese dioxide (used successfully in the "23" process[3]) met this requirement since the cake and any retained uranium could be dissolved in a mixture of nitric acid and peroxide and the uranium subsequently recovered by solvent extraction. In addition, increased decontamination of the uranium solution may be expected since manganese dioxide will adsorb large amounts of gamma activity.[5,6]

Semi-works studies by other workers[2] had indicated the possibility of using MnO_2 as a filter aid in the 25 process. However, in experimental filtrations with MnO_2 in the "25" pilot plant, the filtering time for a batch of dissolver solution was increased by a factor of four to five over that obtained with no filter aid. Before any further work on this problem was carried out on a pilot plant scale, it was decided to study in the laboratory the effect of the variables encountered during filtration.

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3.0 Summary

From the results of laboratory studies, commercial manganese dioxide is advocated as a filter aid in the "25" process. The use of this filter aid increases filtration rates by helping to prevent plugging of filter pores by silica-alumina suspensoids, and permits the use of filter plates with a pore size 3.5 times larger than that used at present. The amount of uranium held up by the manganese dioxide filter aid is small and can easily be recovered. Further investigation on a plant scale is recommended.

Because the filtration rate is very low the use of manganese dioxide co-formed in solution by the action of permanganate on manganous nitrate is not advised. The variation of the percentage MnO (from 0 to 7%) co-precipitated with the MnO_2 was independent of the pH and did not effect the filtering rate. Filtration rates were the fastest when the co-precipitation was carried out in the pH range 0.5-1.95.

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4.0 Experimental and Results

4.1 Filtration with Commercial Manganese Dioxide

An investigation of the filtration characteristics of commercial MnO_2 has been made. The results indicate that uranium hold-up was negligible after washing and that filtration rates were appreciably increased (factor of 3-4) by the use of screened MnO_2 as a filter aid.

By sifting with standard U.S. screens, reagent grade commercial MnO_2 was separated into the following particle size groups:

40% - greater than 177 microns

23% - 62-177 microns

32% - 42-62 microns

5% - less than 42 microns

These percentages were only approximations since accurate separation by screening was not possible. More fines (less than 40 microns) were washed through the 35 micron filter (grade "E") prior to filtration.

It was found that the filtration rate was governed by the amount of the smallest (42-62 microns) group size present. The use of particles (fines) less than 40 microns was not practical since they cause virtual plugging of the filter and should be removed either by decantation or by washing on the filter plate. One sample, composed of 1/3 each of the three group sizes, gave satisfactory characteristics i.e. fast filtration and noncompressibility of the cake (see Table 4.1-1). This sample represented approximately the MnO_2 particle size composition that would be obtained by using all commercial reagent grade MnO_2 that would not pass a 42 micron screen, and could be bought according to such a specification. This size group was selected for further study.

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Table 4.1-1

Effect of Particle Size of Commercial MnO_2 on Filtration Rate

Conditions:

Filter Aid:	Sieved MnO_2
Liquid Filtered:	Water
Δ p:	11.75 pounds
Filter Disc:	"E" Grade (35 micron) micro-metallic stainless steel filter

Samples	MnO_2 Particle Size in Microns	Depth of cake in in/gm/in^2	Filtration Rates in Gal/min/in^2 Gms/ MnO_2/ in^2 Filter 1	3	5
A	>172	0.10	>1	>1	>1
B	62-172	0.06	>1	>1	0.44
C	42-62	0.03	0.04	0.007*	0.003
D	1/2A, 1/2B	-	-	-	>1
E	1/2B, 1/2C	-	-	-	0.48
F	1/3A, 1/3B, 1/3C	-	-	-	0.44

* This figure was 0.009 gal/min/in^2 at Δp = 14.3 lbs. The value of 0.007 was reproduced after the Δ p = 14.3 run, showing the cake to be of a non-packing character.

The hold-up of uranium by screened commercial MnO_2 after washing with 5 cake volumes of hot 1.3M $Al(NO_3)_3$, pH 1.1, was found to be 0.16 mg U/gm MnO_2/ gm U/1. The volume for each wash (15ml) was made sufficiently large to cover the cake. It was evident that the hold-up could be materially reduced by more washing since uranium was still being removed at the end of the 5th wash at the

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rate of 0.1 mg/ml.

Filtration rates in the presence of alumina-silica suspensoids was determined in the following manner: A suspension of hydrous alumina and silica was prepared by adding aluminum nitrate to dilute solutions of sodium silicate with rapid stirring. This slurry, containing silica in suspension and in solution, was used to spike the 1.3M $Al(NO_3)_3$ stock solution used for filtration experiments. The filtration time was decreased by a factor of approximately 4 if screened MnO_2 was used as a filter aid on an "E" (35 micron) filter plate. In all runs using the screened MnO_2 as a filter aid, filtering was continuing at a steady rate after passage of 250 ml. Using unscreened MnO_2, or no filter aid at all, dropwise filtration resulted, indicating that the filter was virtually plugged (see Table 4.1-2).

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Table 4.1-2

Effect of Commercial Screened MnO_2 as a Filter Aid on Filtration Rates

Filter Aid:

Sieved MnO_2: 1/3 42-64 micron particle size

1/3 64-172 micron particle size

1/3 172 micron particle size

"G" grade = Micro metallic stainless steel filters 10 micron pore size

"E" grade = Micro metallic stainless steel filters 35 micron pore size

Run No. 1	Initial Conc. of SiO_2 present (mg/250 ml)	Filter Plate Grade	Filter Aid 4.5 gm/in^2	Conc. of SiO_2 in Filtrate (Mg/250 ml)	Filtrate Appearance	Filtration time/250 ml (min.)
1	6.2	G	None	2.3	Clear	11.5
2	6.2	E	sieved MnO_2	2.8	Clear	3.0
3	6.2	E	Unsieved MnO_2	3.3	Clear	10.
4	6.2	E	None	5.5	Cloudy	0.5
10A	9.8	G	None	-	Clear	9.5
10B	9.8	G	sieved MnO_2	-	Clear	7.5
10C	9.8	G	Unsieved MnO_2	-	Clear	16.

4.2 Filtration with Co-formed MnO_2

Because of the slow filtration rates and the large volumes of wash solution required, the use of co-formed MnO_2 is considered impractical as a filter aid for actual operating conditions.

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Studies with co-formed MnO_2 as a filter aid indicate that the optimum procedure is as follows: Adjust the 25 process solutions to the pH range of 0.5 to 1.9 and heat to 90°C. Add $Mn(NO_3)_2$ to the solution and then add $KMnO_4$ in the ratio of 4 moles of permanganate per 11 moles of $Mn(NO_3)_2$. Digest with agitation for one-half hour at 90°C and filter quickly at the same temperature.

The amount of uranium hold-up in co-formed MnO_2 was found in previous investigations[2,4] to be ca. 0.02 mg U/gm MnO_2/gm/U/l. after a maximum amount of washing with 1.3M $Al(NO_3)_3$ (125-500 cake volumes).

Experiments were carried out to determine the interdependence of the pH of $Al(NO_3)_3$ before the MnO_2 is co-formed, the concentration of the MnO formed, the digestion time, and the filtering rate of the $Al(NO_3)_3$ - MnO_2 slurry. In one series of filtrations the digestion time was kept constant while the pH of the $Al(NO_3)_3$ solution before co-precipitation of MnO_2 was varied from 0 to 2.15 by the addition of HNO_3 or NH_4OH. The same medium porosity sintered filter was used in each run of this series in an effort to maintain uniformly controlled conditions. (see Table 4.2-1 and 4.2-2).

Filtration rates were the fastest and essentially constant when precipitation was carried out in the pH range 0.5 to 1.95. At a pH lower than 0.5 an amorphous precipitate was obtained which increased the filtering time by a factor greater than 3, although it carried less Al than at higher pH values. Precipitation at a pH greater than 1.95 increased the filtering time by a factor of 2 since almost twice as much aluminum was co-precipitated as in the range 0.5 to 1.95.

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Effect of Solution pH on Filtration Rate with CO-formed MnO_2 as a Filter Aid

Conditions:

MnO_2 formed by slow addition of 0.31 M $KMnO_4$ to 1 liter 1.3M Al $(NO_3)_3$ (90°C) containing Mn^{++}

Mole ratio $\frac{KMnO_4}{Mn(NO_3)_2} = \frac{4}{11}$

Digest 1 hr. at 90°C.

Filter at 85° through heated, sintered, medium porosity Gooch at 30-35 mm. Hg vacuum.

			Filtering Time (Minutes)	
pH before Precipitation of 1.5 g MnO_2/l	pH 5 min. after Precipitation of MnO_2	Filtrate pH	1st 250ml	Total 500 ml
0.0	0.02	0.0	-	95
0.25	0.31	-0.22	17	87
0.50	0.30	0.10	11	33
0.75	-	0.22	12	35
1.00	0.58	0.34	11	34
1.25	0.73	0.38	13	67
1.50	-	-	11	44
1.75	-	1.18	10	35
1.90	-	1.45	-	31
1.95	-	1.60	-	32
-	-	-	-	-
2.15	-	1.83	-	75

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In a second series of experiments the pH of the original 1.3M $Al(NO_3)_3$ solution was held constant at 0.83 while the digestion time was varied (see Table 4.2-3). The accuracy of the filtering time, as determined by reproductibility was 33 ± 3 min. for 500 ml. of solution filtered.

Digestion of the precipitate at 90°C for one hour gave shorter filtration times than digestion for 5 minutes or 24 hours. Adjusting the pH with ammonium hydroxide to 1.5 after one hour of digestion did not change the filtering rate if the neutralization were followed by a further digestion and stirring period of one-half hour. Shorter (5 minutes) or longer (24 hours) periods of additional digestion resulted in lower filtration rates. There was apparently no correlation between the rates of filtration and the amount of MnO co-formed with the MnO_2.

X-ray diffraction analyses of the co-formed MnO_2 precipitates showed the presence of manganous manganite crystals of the general formula MnO_2. (0-1) $MnO.n\ H_2O$. The reactants were therefore mixed in the proportions shown in the following reaction (treadwell and Hall, "Analytical Chemistry" Vol. II):

$$4\ KMnO_4 + 11\ Mn(NO_3)_2 + 14\ H_2O \longrightarrow 4\ KMO_3 + 18\ HNO_3 + 5\ Mn(HMnO_3)_2$$

However, the filtrates were found to contain ca. 50% excess of $Mn(NO_3)_2$ which indicated that under these conditions (as listed above) the reaction ratio of $Mn(NO_3)_2$ to $KMnO_4$ varied from about 3/2 to 4/3 depending on the amount of MnO formed. The variation of the percentage MnO (from 0 to 7%) co-precipitated with the MnO_2 was independent of the pH and did not affect the filtering rate (see Tables 4.2-1 and 4.2-2). In a preliminary run, $Mn(NO_3)_2$ was added to a 1.3M $Al(NO_3)_3$ solution containing $KMnO_4$ resulting in a yellow, colloidal filtrate. However, the filtrates from the series in which the permanganate was added to the $Mn(NO_3)_2$ - $Al(NO_3)_3$ solution were all clear.

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Table 4.2-2

Effect of Concentration of MnO and Al in Co-formed MnO_2 on Filtration Time

Conditions:

MnO_2 formed by slow addition of 0.31M $KMnO_4$ to 1.3M Al $(NO_3)_3$ (90°C) containing Mn^{++}.

Mole ratio $\frac{KMnO_4}{Mn(NO_3)_2} = \frac{4}{11}$

Digest 1 hr. at 90°C.

Filter at 85° - 90° through heated, sintered, medium porosity gooch at 30-35 mm. Hg. vacuum.

Wash with hot H_2O and dry ppt. at 110°C for 24 hours.

Composition of MnO_2 Cake				Filtration Time (Minutes)	
MnO%	Al%	MnO_2%	Mn%	First 250 ml.	Total for 500 ml
0	2.43	84.85	52.5	-	95
2.54	1.03	78.98	51.87	17	87
2.70	8.75*	30.76	21.51	11	33
0	4.85	64.41	40.35	12	35
1.94	2.69	66.58	43.50	11	34
7.07	5.88	45.68	34.33	13	67
0	3.95	61.03	38.13	11	44
0.86	3.38	73.54	47.12	10	35
-	-	-	-	-	31
0	4.0	69.13	43.88	-	32
6.85	7.65**	14.41	11.61	-	-
-	13.8**	-	-	-	75

* High because of incomplete washing as a result of cracked cake.

**Ppt. not washed with water.

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Table 4.2-3

Effect of Digestion Time on Filtration Rate with Co-formed MnO_2 as Filter Aid

Conditions:

1. 1.5 gms. MnO_2/liter
2. pH 0.83, adjusted with HNO_3 or NH_4OH
3. MnO_2 formed by slow addition of 0.31M $KMnO_4$ to 1.3M $Al(NO_3)_3$ (90°C) containing Mn^{+2}
4. Mole ratio $\frac{KMnO_4}{Mn(NO_3)_2} = \frac{4}{11}$
5. Digest 1 hr. at 90°C
6. Filter at 85° - 90° through heated, sintered, medium porosity gooch at 30-35 mm Hg vacuum (different gooch than used for table 4.2-1)
7. Wash with hot water
8. Dry ppt. at 110°C for 24 hours.
9. Volume treated = 250 ml.

Run NO.	Digestion Time	Filtering Time Min/250 ml	Composition of MnO_2 Cake			
			% Mn	% MnO_2	% MnO	% Al
14	5 min.	21	25.44	40.50	0	11.0
13	1 hr.	13	41.9	74.25	0	4.67
15	24 hr.	19	48.75	77.79	0	1.66
After 1 Hr. digestion adjust pH to ca. 1.5 with NH_4OH						
Run NO.	Additional Digestion					
16	5 min.	17	36.71	58.13	0	6.5
17	30 min.	13	27.75	42.78	0	9.6*
18	24 hr.	34	26.87	42.37	0	9.6*

* Not washed with H_2O

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4.3 Co-formed MnO_2 Prepared by Alternate Laboratory Methods as a Filter Aid

The material presented in this section represents a limited investigation of the filtration characteristics of MnO_2 formed by other chemical reactions. A slurry containing washed MnO_2 formed by these reactions could be added to "25" dissolver solution for use as a filter aid.

Glycerine (10% in water) was added to a dilute neutral solution of potassium permanganate (90°C) in water and digested for one-half hour forming large flocs of MnO_2. However, only the finest filter (i.e. 10 micron) would hold this precipitate. The filtration rate was very slow.

In another experiment, solid potassium bromate was added to a hot dilute solution of $Mn(NO_3)_2$, 8N in HNO_3, and digested for one-half hour. The resulting precipitate was granular and passed through a 25 micron filter. It was held on the ten micron filter and showed a reasonable filtration rate through the thin cake that was obtained. However, it was felt that due to its small particle size, a thick cake of this material would pack and greatly reduce filtering rates. The screened MnO_2 of particle sizes 42 microns looked much more promising.

In a third experiment solid potassium chlorate was added to a dilute solution of $Mn(NO_3)_2$, 8N in HNO_3 and digested for one-half hour. The precipitate obtained was granular, was held on a 25 micron filter, and exhibited a fast filtration rate for the thin cake obtained. However, due to the inadvisability of using chloride ion in stainless steel equipment, this method was discarded in favor of the screened MnO_2 of mixed particle sizes.

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