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REPORT

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TOPICAL REPORT

A PROCESS FOR CONTROLLING INSOLUBLE URANIUM IN ORE CONCENTRATES

I. Laboratory Investigation

by

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A PROCESS FOR CONTROLLING INSOLUBLE URANIUM IN ORE CONCENTRATES

A process has been developed for converting nitric-acid-insoluble uranium in ore concentrates into soluble form. Ore concentrates are treated with a reducing agent such as carbon monoxide or hydrogen at temperatures of 670-730°C. In the laboratory, retention times required to reach a given level of insoluble uranium vary inversely with the concentration of the reducing agent. Laboratory studies leading to the development of the process are reported.

Introduction

Evaluation of the efficiency of uranium recovery from ore concentrates in the Weldon Spring Refinery raised the question of whether all of the uranium was available to the extracting solvent. Early pilot plant work on the Weldon Spring process at Mallinckrodt Chemical Works¹ had indicated that some concentrates might contain substantial quantities of nitric acid insoluble uranium, and this indication has now apparently been confirmed by the experience of the refinery. Any insoluble uranium lost in the aqueous raffinate is lost permanently from the feed material chain, since there is no further recovery step for this stream.

Siddons and Highfield² of New Brunswick did not find acid insolubility to be a problem in the ten ore concentrates investigated by them in 1955, but construction of new mills and alterations in mill processes made a repetition of their investigation necessary. The program initiated by Mallinckrodt Chemical Works had the following objectives: (1) to determine the extent of uranium insolubility in the various concentrates; (2) to determine the cause of uranium insolubility; and (3) to develop methods for decreasing uranium insolubility losses in plant operation.

Obviously the concept of "insoluble uranium" requires definition. Practically, this term refers to the uranium found in the raffinate of the Weldon Spring refinery in an insoluble form, but the multiple causes of insolubility in the refinery require a more precise definition for laboratory screening purposes. Insolubility in the refinery raffinate may be due to properties of the concentrate (chemical composition, particle size, blending of several concentrates, etc.) and also to the details of the refinery process (digestion time, initial and terminal acid concentrations, cross mixing of streams, etc.). Because of the urgency of the problem, a screening of the various concentrates was begun with an arbitrary technique before a completely definitive procedure for

¹ Krone, L. H., Smith, W. E., and Fariss, R. H., "Pilot Plant Operation of a TBP-Hexane Extraction Cycle for Uranyl Nitrate Purification," *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, MCW-1388 (May 1, 1956), p 9-24

² Siddons, T. J., and Highfield, J. P., *New Brunswick Laboratory: Progress Report*, New Brunswick Laboratory, NBL-127 (July-December, 1955), p 21

the determination of insoluble uranium was worked out. Consequently, the results of the scoping phase in part are semi-quantitative, since the subsequent investigation showed that the arbitrary procedure used for the early part of the evaluation program gave results that were somewhat too high relative to plant experience.

Preliminary Definition of Insoluble Uranium

In principle the uranium found in an insoluble form in the raffinate of a uranium refinery may be due to uranium that has not dissolved in the initial nitric acid digestion and uranium that has precipitated in the course of passage through the refinery operation. A small fraction of the uranium insoluble in the initial digestion operation may dissolve in the course of the process. An initial evaluation was made of a limited number of concentrates to determine qualitatively the cause of the major part of insolubility. This initial evaluation scheme consisted of the following:

A concentrate sample was digested for one hour in 60 per cent nitric acid at 100°C to produce a slurry containing 200 grams of uranium per liter and 3 N excess nitric acid. Two aliquots of the digest slurry were taken. One of the aliquots was filtered, and the residue was washed and analyzed for uranium. This residue represented the digest-insoluble uranium, and the amount present in various concentrates is shown in Column 1 of Table I. The filtrate from the first aliquot was cross-currently extracted with 25 per cent TBP-75 per cent hexane, and the final raffinate was analyzed for uranium. The results from the various feeds are given in Column 2, unextractable uranium, in Table I. The second aliquot of the digest slurry was extracted with TBP-hexane, and the final raffinate was filtered. The cake was washed, and the uranium present represented raffinate-insoluble uranium (Column 3, Table I). The uranium in the filtrate and cake washings represented the soluble but unextracted raffinate uranium (Column 4, Table I). A diagram of the evaluation scheme is shown in Appendix I. The experimental procedure is outlined in greater detail in Part II of this report.³

³ Wise, W., and Stoecker, W., *A Process for Controlling Insoluble Uranium in Ore Concentrates, Part II, Analytical Investigation*, Mallinckrodt Chemical Works, MCW-1423 (February 2, 1959)

Table 1^a

Uranium Content of Digested and Extracted Feed Materials

Feed Material	Total Insoluble Sample Basis %	1 Digest Insoluble U (U basis) %	2 Unextractable U (U basis) %	3 Raffinate Insoluble U (U basis) %	4 Soluble but Unextracted Raffinate U %
Monticello	8.0	0.12	0.003	0.005	0.007
Anaconda (acid leach)	1.6	0.003	0.009	0.0007	0.003
Anaconda	3.8	0.01	0.001	0.0006	<0.001
Uravan	7.0	1.4	0.020	1.3	<0.1
Rifle	0.5	0.006	0.004	0.005	0.006
Rand	3.1	0.004	0.0004	0.0004	0.007
Vitro	8.5	0.08	<0.0008	0.026	0.006
Kerr McGee	1.0	0.02	0.008	0.010	0.016
Naturita	4.3	0.002	0.001	0.002	0.006
Durango	2.5	0.003	0.001	0.0008	0.003
NLO Pilot Plant ^b	8.9	0.01	0.0008	0.065	0.005
Fernald Diuranate ^b	74.6	33.	0.002	24.	0.071
Galigher	13.0	0.07	-	0.07	-

^aData may be in error due to digestion procedure.

^bThese materials are recycle residues, not concentrates.

The results of this experiment are summarized in Table I. Column 1 indicates the fraction of uranium in the concentrate that remained insoluble under the particular acid concentration and digestion time used in the digestion procedure. The second column indicates the quantity of uranium that is unextracted from a filtered digest solution, that is, it shows the extraction efficiency relative to the dissolved uranium. The third column shows the fraction of uranium found in an insoluble form in the raffinate from a slurry that had been solvent extracted. This includes

all uranium insoluble in the initial digest, altered by any precipitation or solubilization occurring during the course of extraction. The fourth column shows the uranium left unextracted in the liquid phase of the raffinate. The results in Table I indicate the presence of both initially insoluble and, to a lesser degree, reprecipitated uranium. On the basis of this work, it was decided to consider as insoluble uranium that fraction of the total uranium in the concentrate which remains insoluble after digestion under predetermined conditions of initial and terminal nitric acid concentration, digestion time, and temperature. The completion of this definition requires establishing values of these experimental conditions. This is the subject of Part II³ of this report, which deals in detail with the development of the analytical method used for measurement of insoluble uranium. The early part of the screening work was done with an arbitrary choice of these experimental conditions.

Evaluation of Ore Concentrates

A systematic evaluation of the nitric acid solubility of the uranium from the various raw materials sources was carried out to identify the chief source of non-recoverable uranium. Analysis of plant experience indicated that the Colorado concentrates apparently contained appreciably more insoluble uranium than any other class of concentrates being processed. Hence, the work summarized in this report is largely concentrated on these domestic mills. The wide variety of primary ores processed and the differing mill processes employed, result in a considerable mill-to-mill variation in the behavior of domestic concentrates in a refinery process; hence, a similar variation in the solubility of contained uranium is to be expected. In Table II are typical analyses of the concentrates screened in this work. In addition to the constituents indicated in this table, aluminum and magnesium are present as minor constituents together with traces of a number of other elements. The selection of these particular concentrates was determined by the types of raw materials processed by the refinery at the time of discovery of the insoluble problem, and Table II does not represent a complete list of current domestic feed materials.

Table II

Composition of Feed Materials Tested

<u>Feed Material</u>	<u>U</u> <u>%</u>	<u>V₂O₅</u> <u>%</u>	<u>P₂O₅</u> <u>%</u>	<u>SiO₂</u> <u>%</u>	<u>SO₄²⁻</u> <u>%</u>	<u>MoO₃</u> <u>%</u>	<u>Fe</u> <u>%</u>
Monticello	55.34	0.05	0.7	6.0	9.3	0.22	2.5
Anaconda (acid leach)	68.6	0.33	0.2	1.4	1.5	.04	0.7
Anaconda (carbonate leach)			0.4	3.5			0.6
Uravan	65.8	2.0	2.3	0.9	5.6	.09	3.7
Rifle	69.9	3.	0.4	0.2	16.3	.04	0.3
Rand	70.4						2.2
Vitro	51.8	1.6	3.5	3.0	2.	.95	2.6
Kerr McGee	67.7	1.3	1.0	0.8	3.5	.45	3.2
Naturita	67.8	0.2	0.1	3.0	1.7	.04	0.7
Durango	75.6	0.1	0.04	1.9	2.5	.02	0.75
NLO Pilot Plant	59.	1.6	0.85	7.1	3.5	.7	1.2
Fernald Diuranate	34.7		9.8	18.8			1.7
Galigher	55.6	0.2	0.6	2.	2.5		2.

Samples of lots of these concentrates were digested in nitric acid, and undissolved uranium was determined by procedure A-1 in the Appendix. Results of insoluble uranium determinations on different lots of concentrate from various vendors are given in Table III. In the later work a modified analytical procedure was used. These modifications in method are discussed in detail in Part II⁹ of this report.

Table III^a

Insoluble Uranium in Feed Materials

Feed	Lot No.	Total U In Digest Slurry g/l	Total Dry Solids in Digest Slurry g/l	Insoluble U Per cent of Total Insoluble	Insoluble U Per cent of Total U
Anaconda	A1109	272	12.0	0.042	0.0009
	A1110	168	3.0	.022	.0004
	A1111	270	2.5	.015	.0001
	A1115	264	5.5	.052	.0001
	A1118	239	6.5	.047	.0001
Durango	514	299	26.5	.35	.032
	513	360	29.0	.36	.029
	515	334	12.5	1.01	.035
	518	307	8.0	0.108	.003
	519	334	12.	.136	.005
Monticello	A 119	202	40.	.020	.004
	A 120	232	36.	.015	.002
	A 123	253	26.	.014	.001
	A 122	246	24.	.021	.002
	A 124	217	32.	.015	.002
	A 125	236	22.	.033	.003
	A 126	222	18.	.039	.003
Rare Metals	61	185	3.5	.016	.0003
	62	214	4.5	.018	.0003
Uranium Reduction	269	287	46.0	.39	.063
	270	288	56.	.32	.062
	268	320	29.	.92	.087
	283	396	25.	.18	.011
	285	402	30.	.083	.006
	272	342	50.	.79	.12
	273	268	23.	.065	.005
	279	266	12.	.078	.004
	274	256	23.	.18	.016
	275	300	31.	.45	.047
	276	240	34.	.16	.023
	280	290	20.	.17	.012
	281	292	22.	.45	.034
	282	216	18.	.090	.008
	284	303	32.	.30	.031
	319		16.		.15
	321		12.		.053
	322		28.		.09
	323		26.		.26
	324		17.		.098
	325		11.		.069

Table III (continued)

Feed	Lot No.	Total U In Digest Slurry g/l	Total Dry Solids in Digest Slurry g/l	Insoluble U Per cent of Total Insoluble	Insoluble U Per cent of Total U
Uranium Reduction	326		12.		.18
	328		11.		.045
	329		13.		.14
	330		14.		.21
	331		16.		.18
	332		11.		.13
Vitro ^{b, c}	56	245	43	.37	.065
	57	336	67.	.35	.070
	58	229	111.	5.4	2.60
	59	226	98.	4.4	1.90
	60	209	102.	11.4	5.50
	61	274	56.	4.2	0.86
	62	252	42.	5.8	.96
	65	251	127.	18.9	9.60
	67	282	95. (28.)	18.9	6.40 (13.40)
	68	250	118. (33.)	2.7	1.30 (1.67)
	63		(21.)		(4.00)
	64		(20.)		(4.90)
	66		(23.)		(5.80)
	69		(37.)		(8.00)
	70		(31.)		(5.00)
	71		(19.)		(5.40)
	72		(25.)		(7.10)
	75		(28.)		(11.80)
	77		(9.9)		(1.13)
Dawn	2	227	5.5	0.010	0.0002
Western Nuclear	5	222	105.0	.014	.007
	6	206	100.	.011	.005
	7	229	45.	.0081	.0063
	9	336	32.	.008	.0008
	10	249	39.	.012	.002
	11	216	28.	.021	.003
	12	242	25.	.014	.002
Rifle	R 44	308	4.	~8.0	.10
	R 40	286	4.	~5.	.07
	38	318	78.	~6.1	.15
	41	265	8.	4.1	.12
	45	314	1.5	4.2	.019
	48	305	16.0	10.2	.52
	49	308	4.5	8.5	.12

Table III (continued)

Feed	Lot No.	Total U In Digest Slurry g/l	Total Dry Solids in Digest Slurry g/l	Insoluble U Per cent of Total Insoluble	Insoluble U Per cent of Total U
Uravan	629	321	18.0	1.84	.10
	636	282	24.	3.5	.30
	637	242	22.	4.7	.44
	638	284	26.	5.6	.51
	639	300	26.	4.0	.33
	640	249	31.	11.	1.40
	644	284	26.	1.72	0.16
Edgemont	60	306	0.0		
Naturita	371	250	15.	0.075	.004
	372	290	5.	.165	.003
	374	251	6.	.24	.006
Climax ^c	249	286	25. (9.6)	25.5	2.30 (2.90)
	250	284	11. (4.2)	0.24	0.01 (2.79)
	252	319	8. (2.8)	31.5	.81 (1.18)
	253		(2.6)		(1.18)
	254		(1.6)		(0.55)
	256		(6.2)		(3.10)
	257		(3.2)		(1.37)
	258		(1.2)		(0.28)
	259		(3.4)		(.76)

^a Data were obtained before analytical methods of suitable accuracy and precision were developed.

^b Vitro process changed between Lots 58 and 59.

^c Values in parenthesis are from digest slurries containing approximately 1 N excess HNO₃. See Part II of this report for details of the modified digestion procedure.

Results are summarized in Table III. This table provides a qualitative picture of individual mill products and identifies the general level of insoluble material in each raw material. Uranium Reduction, Vitro, Rifle, Uravan, and Climax lots tested contained considerably more insoluble uranium than concentrates from the other vendors, and satisfactory uranium recovery in the plant could be expected only if the insoluble uranium in these

feeds could be controlled. Since very little information was available on the effect of digestion conditions on nitric acid insoluble uranium, these variables were investigated.

Effect of Digestion Procedure

A scoping experiment was carried out on Vitro concentrate to determine whether minor variation in digestion procedure could lead to a solution. The experiments summarized in Table IV were done to show the effects of digestion time, terminal acidity, and feed blending on the nitric acid insoluble content of Vitro feed. Edgemont concentrate, which contains no insoluble uranium, was blended with Vitro concentrate to give samples containing 30 per cent Vitro-70 per cent Edgemont and 10 per cent Vitro-90 per cent Edgemont. Digestion times were 1, 6, and 36 hours. Nitric acid concentrations were 1, 3, and 6 *N* excess. The results of this experiment are shown in Table IV.

Table IV

Effect of Digestion Time, Terminal Acid, and Feed Blend
on the Nitric Acid Insoluble Uranium Content of Ore Concentrate

(The result reported in each block is per cent insoluble uranium based on the uranium content of the Vitro fraction of the sample only, since the uranium in the Edgemont material is entirely soluble.)

Feed Blend	Digestion Time								
	1.0 Hour			6.0 Hours			36 Hours		
	Approx. 1M	Excess 3M	HNO ₃ 6M	Approx. 1M	Excess 3M	HNO ₃ 6M	Approx. 1M	Excess 3M	HNO ₃ 6M
100% Vitro	1.98	1.63	1.36	1.22	0.93	0.74	0.77	0.71	0.61
	1.91	-	-	-	0.91	-	-	-	0.58
30% Vitro —									
70% Edgemont	1.61	1.16	1.04	0.87	0.92	0.81	0.75	0.79	0.69
	-	1.20	-	-	-	0.765	0.805	-	-
10% Vitro —									
90% Edgemont	0.99	0.76	0.65	0.65	0.61	0.68	0.85	0.64	0.55
	-	-	1.04	0.77	-	-	-	0.63	-

The results of Table IV show that the effects of terminal acidity and feed blending decreased with increasing digestion times, indicating that time of digestion was the most critical variable in this experiment. However, the magnitude of the improvement was insufficient for production purposes.

The result of this experiment generally agreed with earlier preliminary work on Uravan concentrates⁴ which had indicated that the grinding of the concentrate, longer digestion time and the addition of some hydrochloric acid to the digest acid, would decrease the amount of insoluble uranium slightly, but to an extent insufficient to provide a process. It was concluded that the uranium is probably included in other insoluble material, and is not exposed to the digest liquor. Although grinding to a particle size finer than 100 mesh was considered as a solution to the plant problem, the increased operating cost which would result made it desirable to continue the investigation.

Investigation of Cause of Insolubility

Preliminary investigations at the Winchester Laboratory⁵ and at Mallinckrodt⁶ indicated that the insoluble uranium content of a concentrate was dependent both upon its chemical composition and the temperature at which it was dried. Since all of the high-insoluble uranium concentrates were made by a process involving a roast, the effects of temperature and time were investigated.

Samples of two lots of Uravan (high-insoluble uranium) and one lot of Durango (low-insoluble uranium) were ignited for 3 hours in air at temperatures in the range 150 to 650°C. The roasted samples were then analyzed for insoluble uranium with the results in Table V. One lot of Uravan showed a significant increase in insoluble uranium after roasting above 350°C. The Durango concentrate remained free of insoluble uranium throughout the temperature range.

⁴ Lang, G. P., and Martin, G. L., "Insoluble Uranium in Feed Materials," *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1401 (April 1, 1957), p 13-16

⁵ Lindstrom, R. W., Private Communication

⁶ Lang, G. P., Varwig, J. W., and Martin, G. L., "Insoluble Uranium in Feed Materials," *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957), p 13-20

Table V
The Effect of Ignition Temperature on Insoluble Uranium

Ignition Temperature °C	Insoluble Uranium, U-Basis		
	Uravan Lot 477 %	Uravan Lot 478 %	Durango Lot 452 %
150	-	0.65	0.0023
250	0.70	0.53	.0019
350	.78	0.68	.0008
450	.80	0.95	.0013
550	.88	1.25	-
650	.87	-	.0023

A more striking example of the effect of roasting was observed with Vitro material. Samples of wet concentrate filter cake (this wet cake is roasted at 300 - 600°C to produce the Vitro concentrate) were roasted in air for three hours at various temperatures with the results shown in Table VI and in Figure 1. The insoluble uranium content increases sharply at calcination temperatures of 400-500°C and drops rapidly at temperatures above 800°C. Lindstrom⁵ has found the same relationship between uranium insolubility and calcining temperature in concentrates from Climax, Shiprock, Moab, Tuba City, Rifle, Anaconda (acid) and Monticello (acid). Anaconda carbonate and Monticello carbonate concentrates, on the other hand, did not show a maximum in the temperature-insolubility curve.

Table VI

The Effect of Calcining Conditions on Insoluble Uranium

Feed	Calcining Temperature °C	Total Dry Solids per cent	Insoluble U Per cent of Total Insoluble	Insoluble U Per cent of Total U	Chloride after Calcining per cent
Vitro Wet Cake	No Calcining	0.5	9.0	0.05	2.05
Vitro Wet Cake (water leached)	160	2.3	1.75	0.05	0.72
Vitro Wet Cake (water leached)	215	2.9	1.83	0.06	0.90
Vitro Wet Cake	300	11.1	2.04	0.25	2.0
	400	9.7	3.24	0.32	1.1
	500	16.4	13.8	2.24	0.14
	600	20.0	15.3	3.05	0.14
Vitro Wet Cake (Pre-dried 16 hours at 110°C)	600	21.8	15.3	3.30	
Vitro Wet Cake	700	22.4	11.2	2.48	0.06
	800	27.0	19.6	5.12	
	900	21.6	0.79	0.16	
	1000	20.6	0.61	0.12	
Vitro Wet Cake (Hydrogen atmosphere)	600	2.4	0.81	0.02	0.60 ^a
Vitro Lot 60 (Hydrogen atmosphere)	600	8.4	0.72	0.11	
Vitro Lot 65 (Hydrogen atmosphere)	600	7.5	0.26	0.03	

^a High chloride probably due to the small exit tube in the closed system and the shorter ignition time.

Figure 1

EFFECT OF CALCINING TEMPERATURE ON INSOLUBLES IN VITRO WET CAKE

The results of Figure 1 suggest that use of either low or very high roasting temperatures could be used to reduce insoluble uranium in Vitro concentrate. The high temperature solution was considered impractical because of the type of calcining equipment used by the mills. Lower calcination temperatures on the other hand were insufficient in the case of Vitro material to produce a chloride free concentrate (Table VI). Precipitation of the wet cake is from a chloride solution in the Vitro process, and the calcining operation is necessary to produce a concentrate meeting both the chloride specification (0.1% on uranium basis) and the assay limit (75% U_3O_8) in the final product. It is interesting to note that the total quantity of acid insoluble matter did not decrease when a calcining temperature greater than 850°C was used despite the decrease in insoluble uranium.

In contrast to the air calcines, roasting in a hydrogen atmosphere at moderate temperatures produced a product containing a greatly reduced insoluble uranium content. The acid insoluble residue from reduced, roasted concentrate showed X-ray diffraction lines of magnetite instead of the hematite⁷ seen in the acid insoluble residues from concentrates made at temperatures below 800°C. The concentrates roasted above 800°C also showed an acid insoluble residue containing magnetite. A reductive roast provided a possible plant process for recovery of insoluble uranium if it could be used to solubilize already fixed material.

Reduction Roasts

A composite sample of Vitro lots 63, 64, 66, 67, 70, 71, 72, 75, and 77 was used to investigate the effect of a reduction roast on a concentrate that had been given an oxidizing roast and contained insoluble uranium.

Samples of this composite were heated for various times at temperatures between 150 and 600°C. The sample was heated to the desired temperature in argon and a flow of hydrogen introduced (2.5 liters/min) for the indicated time. Samples were then cooled to room temperature as quickly as possible in argon and analyzed for insoluble uranium by method A-3 in the Appendix. The results covering a variety of time-temperature conditions are given in Table VII.

⁷ Spectrographic analyses of the acid insoluble residues from a few lots of Vitro, Uravan, and Gallagher concentrates showed the presence of uranium, iron, and silicon as major constituents, with various other elements present in trace quantities. X-ray powder diffraction patterns contained lines characteristic of SiO_2 and Fe_2O_3 (hematite). In addition, an unidentified diffraction pattern (d spacings: 5.10, 4.08, 3.27, 2.60, 2.03, 1.84, and 1.74) that resembles patterns given by uranates and ferrites was seen.

Table VII

Insoluble Uranium in a Vitro Feed Composite After Calcining in a Hydrogen Atmosphere
(Effect of Retention Time and Temperature)

Calcining Time hours	Temperature °C	Total Solids %	Insoluble U % (U basis)	Excess HNO ₃ N	HNO ₃ Consumption g/g
0	-	22.4	5.75	-	0.46
(2 of 9 lots)					
2.0	625	1.6	0.006	1.4	1.03
2.0	576	4.2	0.013	2.1	0.93
2.0	500	3.8	.029	2.8	0.83
1.0	738	1.2	.010	1.1	1.07
1.0	730	1.2	.008	1.4	1.03
1.0	672	1.3	.003	1.8	0.97
1.0	635	2.2	.013	0.8	0.99
1.0	602	2.8	.013	1.2	0.93
1.0	500	6.3	.24	2.2	0.79
0.5	688	1.2	.003	1.3	1.03
0.5	625	3.3	.013	2.1	0.93
0.5	586	3.1	.017	1.5	0.97
0.5	553	3.6	.019	2.0	0.90

At temperatures above 500°C excellent solubilization was obtained in all experiments. At 500°C a retention time greater than 2 hours was necessary to produce the same effect.

A similar decrease in insoluble uranium was observed in an experiment in which carbon monoxide was used as a reducing gas in place of hydrogen. The results are shown in Table VIII. On the basis of the results of Table VII and VIII, operating temperatures of 670-700°C for a hydrogen roast and 670-730°C for a carbon monoxide roast, and a reduction time of one-half hour were selected as a procedure. Use of this process reduces the quantity of insoluble uranium by a factor of 100 to 1000. The reducing roast was also applied to samples of individual lots of Vitro, Climax, Rifle, and UraVan concentrates that

were known to contain large amounts of nitric acid insoluble uranium and was found to be uniformly applicable to those concentrates. Nitric acid consumption was more than doubled by the reduction treatment, but most of the additional acid could be recovered in refinery operations. Table IX shows the effects of the reducing roast on Vitro, Climax, Uravan, and Rifle concentrates.

Table VIII

Insoluble Uranium in a Vitro Feed Composite
After Calcining in a Carbon Monoxide Atmosphere
(Effect of Retention Time and Temperature)

Calcining Time hours	Temperature °C	Total Solids %	Insoluble U % (U basis)	Excess HNO ₃ N	HNO ₃ Consumption g/g
0	-	22.4	5.75	-	0.46
1.0	730	3.2	0.007	0.95	.98
1.0	668	4.9	.016	1.35	.95
1.0	616	5.8	.040	1.15	.95
1.0	581	5.9	.057	1.4	.92
1.0	516	6.0	.099	1.75	.87
0.5	680	5.9	.023	1.85	.86

Table IX

Insoluble Uranium and Total HNO_3 Insoluble in Ore Concentrates
Before and After Calcining in H_2 or CO Atmospheres^a

Feed	Lot Number	Per cent Total HNO_3 Insoluble			Per cent Insoluble Uranium (U basis)		
		Original	H_2 Reduced	CO Reduced	Original	H_2 Reduced	CO Reduced
Vitro	61	21.	6.0	-	1.3	0.025	-
	62	8.4	7.0	-	1.0	.039	-
	63	21.	5.2	-	4.0	.010	-
	64	20.	12.	-	4.9	.038	-
	66	23.	1.8	-	5.8	.007	-
	67	28.	0.13	-	6.4	.0005	-
	68	24.	8.8	-	1.4	.051	-
	69	37.	9.9	-	7.7	.078	-
	70	31.	4.7	-	5.0	.017	-
	73	37.	10.	7.8	14.9	.197	0.129
	74	21.	3.6	-	5.8	.089	-
	77	10.	0.21	-	1.4	.001	-
	79	8.2	0.3	0.4	1.2	.0004	0.004
	82	6.2	0.6	0.8	1.1	.003	0.004
	89	24.	8.8	-	4.5	.062	-
Climax	256	6.2	0.6	-	3.1	.031	-
	257	3.2	0.7	-	1.4	.025	-
	259	3.7	1.1	-	1.1	.005	-
Uravan	640	6.2	1.2	-	1.4	.003	-
	648	8.0	1.4	-	1.4	.002	-
Rifle	R48	3.1	1.1	-	0.5	0.36	-

^a In all cases the retention time was one hour at 625°C ; H_2 or CO flow was 2.5 liters per minute.

All of the data in Tables VII, VIII, and IX were obtained using pure hydrogen or carbon monoxide as a reductant. In actual plant operation, the source of the reductant would probably be either cracked ammonia or a reducing gas flame. For this reason some laboratory reduction runs were made using gas mixtures. To simulate cracked ammonia, a three-to-one volume ratio of hydrogen was used. In the case of a reducing gas flame, it is more difficult to calculate or determine the composition of the gas mixture, so a series of empirical experiments was carried out with a reducing flame.

Reduction Roast with Reducing Flame

Gas-flame reduction runs were carried out in a reduction chamber, a sketch of which is shown in Figure 2. Two gas-air torch tips were sealed into the chamber through the face plate. The torch tips were placed at right angles so that the smaller burner could function as a pilot burner while the main burner was operated with deficient oxygen. Both the gas flow (a 40% propane-air mixture) and air flow were measured with rotameters. Analyses with a standard Orsat apparatus were made of the combustion product gas from various fuel-air mixtures in the optimum temperature range for concentrate reduction. The results are shown in Table X.

Table X

Analyses of Reducing Gas at Various Fuel-Air Mixtures

Oxygen/Propane Ratio	Temperature °C	Total Input Flow Rate l/min.	Product Gas Analysis				
			CO ₂ %	CO %	O ₂ %	H ₂ %	Illuminants %
2.3	~ 120	10	2.0	4.4	13.3	-	-
2.3	690	10	6.2	7.6	2.7	-	~ 6.
2.3	702	10	5.0	6.7	5.4	4.7	5.
3.06	680	13	8.4	6.9	0.4	-	5.
3.06	670	10	8.6	4.8	2.9	-	5.
3.06	685	10	4.3	7.9	2.6	5.0	2.
3.8	685	10	9.0	4.5	2.6	-	4.
3.8	685	10	5.8	3.7	0.7	4.8	1.
3.8	700	10	4.0	7.0	6.7	3.7	3.
4.56	694	10	5.3	10.6	2.6	-	3.
4.56	692	10	8.0	7.0	2.3	-	-
4.56	685	10	2.7	10.2	0.7	8.1	<1.
5.3	706	10	8.6	6.6	2.3	-	~1.
5.3	670	10	2.6	4.3	2.3	4.8	0.

Figure 2

GAS-FLAME REDUCTION CHAMBER

Although there is considerable variation in the results, they do indicate that the combustion products of the air-propane flame will contain about 5 per cent of both carbon monoxide and hydrogen. The literature data on the combustion of natural gas and acetylene are consistent with this result. The concentrations of carbon dioxide, carbon monoxide, hydrogen, and water in the product gas will be governed by the water gas shift reaction, which has an equilibrium constant of approximately one at a temperature of 700°C.

The results of a number of reduction runs with hydrogen diluted with nitrogen in the ratio of cracked ammonia and with carbon monoxide in the concentration that might be expected from a reducing gas flame are shown in Figure 3.

As the concentration of active reducing agent in the reducing gas mixture was lowered, a longer retention time was required to reach a given level of insoluble uranium. This effect was independent of the quantity of excess reducing agent passed over the sample in a given period of time. Three different levels of excess carbon monoxide (5-, 10-, and 20-fold) were used in the reduction runs with 5 per cent carbon monoxide-nitrogen, and all six points appear to define a single curve. Actual gas-flame reductions may not be quite as effective as indicated by the concentrations of carbon monoxide and hydrogen in the product gas because of the presence of unburned oxygen.

Starch and scrap uranium metal were investigated as possible reducing agents. The required amount of starch or scrap metal was mixed with the concentrate, and the mixture was calcined in a laboratory muffle. Tables XI and XII give data on reduction of two different samples of Vitro concentrate by gas-flame, starch, and scrap metal. All of these procedures increased the solubility of the uranium, but they were not as effective as pure hydrogen or carbon monoxide. About 94-95 per cent of the original insoluble uranium was solubilized in the gas flame experiments, and it is probable that with longer retention times the gas flame would be as effective as diluted carbon monoxide.

Figure 3

EFFECT OF RETENTION TIME AND REDUCING GAS COMPOSITION
ON NITRIC ACID INSOLUBLE URANIUM

Table XI

Nitric Acid Insoluble Uranium in Vitro Feed Material^a
After Various Reduction Treatments

Treatment	Calcining Time hours	Temperature °C(± 10°C)	Total Solids %	Insoluble Uranium % (U-basis)	Excess HNO ₃ N	Acid Consumption g/g
None	0	-	24.	4.5	1.2	0.44
2.5 l/min H ₂	1.0	630	8.8	0.062	1.2	0.95
Gas flame ^b	2.0	678	9.4	0.30	1.8	0.87
1.9 l/min gas + 8.0 l/min air						
1.9 l/min gas + 6.0 l/min air	2.0	664	9.5	0.28	1.7	0.88
1.9 l/min gas + 6.0 l/min air	1.0	671	9.2	0.25	1.8	0.87
1.9 l/min gas + 6.0 l/min air	0.5	670-690	9.5	-	1.6	0.89
Calcine with scrap uranium in muffle: 65 g sample + 28.4 g uranium	1.5	670	24.4 ^c	0.86 ^c	4.4	

^a Vitro Lot No. 89

^b The gas used was 40% propane-air mixture. Flow rates quoted are for the principal burner in the chamber.

^c Based on Vitro weight

Table XII

Nitric Acid Insoluble Uranium in Vitro Feed Material^a
After Various Reduction Treatments

Treatment	Calcining Time hours	Temperature °C(±10°C)	Total Solids %	Insoluble U % (U-basis)	Excess HNO ₃ N	Acid Consumption g/g
None	0	-	37.	14.9	2.1	0.33
2.5 l/min H ₂	1.0	635	10.	0.197	1.4	0.92
2.5 l/min CO	1.0	650	7.8	0.129	0.8	1.0
Calcine with starch in muffle: 50 g sample + 25 g starch	0.5	650	14.	0.27	3.8	0.94
50 g sample + 10 g starch	0.5	650	13.	0.40	3.0	1.1
Gas flame ^b 1.7 l/min gas + 11.0 l/min air	0.75	690	17.	0.72	2.9	0.72
1.9 l/min gas + 6.0 l/min air	1.0	650	16.	0.63	2.8	0.73
1.9 l/min gas + 6.0 l/min air	1.0	640	19.	1.15	3.0	0.71
1.9 l/min gas + 11.0 l/min air	0.5	700	17.	0.77	2.6	0.75

^a Vitro Lot No. 73

^b See footnote b, Table XI

Post Reduction Pyrophoricity

In some cases the Vitro concentrate was pyrophoric after the reduction treatment. This was probably due to the rapid oxidation of Fe⁰ to FeO. When Fe₂O₃ is reduced to Fe^c with hydrogen, the metal may be pyrophoric, and the lower the reduction temperature, the greater the tendency toward pyrophoricity.⁸ A pyrophoric product may create a material handling problem, but the

⁸ Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Company, New York (1953), Vol. 13, p 805

partial re-oxidation of the product does not affect the insoluble uranium if the product is cooled to room temperature before exposing to air. If the reduced material is exposed to air while hot, however, some of the uranium is again rendered insoluble. The data in Table XIII indicate that some cooling of the reduced material in a reducing or inert atmosphere is necessary prior to contact with air.

Table XIII

Effect of Pyrophoricity (Post-oxidation) on the Insoluble Uranium Content
of Reduced Vitro Concentrate (Lot 62)

Insoluble Uranium in Unreduced Vitro Lot 62: 1.94%

<u>Treatment After Reduction</u>	<u>Insoluble Uranium %</u>
Exposed to air at 30°C	0.02
Exposed to air at 300°C	.04
Exposed to air at 500°C	.07
Exposed to air at 700°C	.24
Held at 600°C in air for 1 hour	~0.4 ^a

^a Estimate based on a sample (Lot 89) which gained back 20% of its original insoluble uranium content

The experimental work outlined above indicates that a plant process for controlling the amounts of nitric acid insoluble uranium is entirely feasible. Plant scale tests will be reported as another part of this report.

Summary

A feed evaluation program is reported in which concentrates from several mill sites were tested for insoluble uranium. Six of the concentrates tested contained insoluble uranium in amounts greater than 0.01 per cent, and four of the six contained quantities greater than 0.1 per cent.

Studies of the formation of insoluble uranium in concentrates indicate that the amount of insoluble material may be related to the chemical composition of the concentrate and to the temperature at which it is calcined at the mill.

A process has been developed on a laboratory scale for controlling the amount of nitric acid insoluble uranium in ore concentrates. The concentrates are treated with a reducing agent such as hydrogen or carbon monoxide at temperatures of 670-730°C. Data were collected to determine the efficiency of such reducing gases as cracked ammonia and propane-air mixtures. In the laboratory, retention times required to reach a given level of insoluble uranium vary inversely with the concentration of the reducing agent.

APPENDIX I

Method Used in Initial Evaluation of Ore Concentrates

^a Cross-current extraction is defined as the extraction of the same aqueous phase with successive fresh aliquots of solvent. A 1:1 volume ratio was used.

^b Analyses were by x-ray techniques.

APPENDIX II

Method A-1

A 250-gram sample of concentrate was digested in approximately 3 N HNO_3 for one hour under boiling reflux. Two hundred ml of the digested slurry was centrifuged, the clear liquor was removed and discarded, and the insoluble residue was washed by repulping with 5 per cent HNO_3 . The washing procedure was repeated until the centrifugate gave a negative caustic-peroxide test for uranium (6 to 8 washings). The insoluble residue was dried at 110°C , and uranium was determined by X-ray fluorescence.

Method A-2

An accurately weighed, 50.0 g sample of concentrate was transferred to a 500-ml boiling flask, a condenser was connected to the flask, and 50 ml of 45 per cent (w/v) nitric acid was added. The acid was washed down the condenser with 20 ml of distilled water, and the sample was digested at $91\text{--}95^\circ\text{C}$ for two hours with mechanical stirring. After cooling, the slurry was centrifuged at 1750 rpm for 15 minutes. The liquid was decanted, and the solids were washed successively with 50-ml and 25-ml portions of distilled water, centrifuging the slurry and decanting the liquid each time. The solids were then repulped with 25 ml portions of 5 per cent (v/v) nitric acid until the centrifugate gave a negative test for uranium with alkaline hydrogen peroxide. (About 5 washings were required.) The solids were dried over night at 110°C , after which they were analyzed for uranium by X-ray methods.

Method A-3

Eighty-gram samples were digested in sufficient nitric acid and water to produce a digest slurry with a terminal acidity of approximately 1 N HNO_3 and a uranium concentration of approximately 400 grams per liter. The slurry was digested under reflux for approximately one hour. The solids were centrifuged and washed with 5 per cent HNO_3 until the alkaline peroxide test for uranium was negative. The solids were dried at 110°C , and uranium was determined by X-ray methods.