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STUDIES OF RECOVERY PROCESSES FOR WESTERN URANIUM BEARING ORES

Part I
A CRITICAL EXAMINATION OF THE SALT-ROAST, ACID-LEACH PROCESS FOR WESTERN URANIUM ORES

Part II
DIRECT ACID LEACHING OF WESTERN URANIUM ORES

By V. L. SAINE and K. B. BROWN

Y-12 PLANT

CARBIDE AND CARBON CHEMICALS CORPORATION

OAK RIDGE, TENNESSEE

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STUDIES OF RECOVERY PROCESSES FOR WESTERN URANIUM-BEARING ORES

FOREWORD

Uranium is an abundant element. Yet the quantities of this material which have been found in high-grade ores such as pitchblende are comparatively small. In the United States, where essentially no pitchblende deposits have been discovered, the most accessible supply of uranium is in the form of fairly low-grade carnotite ores. Consequently, a development of the carnotite fields in the Colorado Plateau is being organized by the Raw Material Division of the Atomic Energy Commission.

Small scale processing of the Western ores has been conducted for many years in plants operated by the U.S.Vanadium Corporation, and the Vanadium Corporation of America, using two different processing methods which will be referred to hereafter as the "acid-process", and the "carbonate-process". It has been the natural practice in these plants to process a rather select group of ores, which are known to yield the greatest amount of product for effort expended (namely, carnotites or roscoelites of high vanadium and low-lime content). Also, at least prior to the second World War, the primary interest at these plants has been concentrated on vanadium.

In a program for full exploitation of the Western ores for uranium, it will not always be possible to pick and choose the ores to be treated. As a consequence, since the deposits vary rather widely in com-

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position, a number of processing problems are bound to arise. The existing processes are exceedingly important, of course, and the extent or limitations of their application to the variety of ores should be thoroughly understood. In addition, however, it will eventually be necessary to produce new and improved methods for milling practice.

Studies of the Western ores have been assigned by A.E.C., Raw Materials Division, to Y-12 and other research centers. This work was initiated at Y-12 during July, 1948, with two objectives: (1) to develop familiarity with the salt-roast, acid-leach method ("acid-process"), as now practiced at Rifle, Colorado; to determine the optimum conditions for operation; and to explore its applicability to Western ores in general; and (2) to develop new lines of research looking toward an improved, or perhaps entirely new, methods for recovery of uranium from the Colorado Plateau ores. In April, 1949, development work on certain aspects of the carbonate process[1] was also assigned to these laboratories.

At this time, the studies of the salt-roast, acid-leach (Rifle) process are essentially complete. It is the purpose of this report (PART I) to present a full summary of the work performed on that program. In addition, investigations have been made of the application of direct acid

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(1) The salt-roast, carbonate-leach process has been studied by the Bureau of Mines, Salt Lake City Branch and by Battelle Memorial Institute. Recently, investigations of certain solution Chemistry problems have been assigned to Y-12. For background information, a simplified flowsheet for this process is given in Appendix C.

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leaching methods to the Western ores. Since it is sometimes advisable to review the two types of processes in parallel, data for the direct leaching tests are also presented in the following sections (PART II). Summaries of other phases of the carnotite program (e.g., Recovery of Uranium and Vanadium for Acid Liquors) will be reported in separate documents.

A more detailed presentation of the information on which this report is based has been submitted in monthly progress reports starting with July, 1948, and continuing through July, 1949. A complete list of these reports is given in Appendix A.

DESCRIPTION OF ORES

Carnotite and roscoelite ores are made up primarily of silica as sand grains with a matrix and partings of fine, clay-like materials containing the mineral values and bases. Chemical analyses for several different ores which have been studied at these laboratories are presented in Table 1.

Uranium exists in the ores as the mineral, carnotite (hydrous potassium uranyl vanadate). Vanadium is accounted for partly by this mineral but mostly by deposition of vanadyl vanadates, calcium vanadates, and vanadium micas. In roscoelite ores, the vanadium exists almost entirely as vanadium micas. Calcium and magnesium are present mainly as calcite and dolomite, and additional bases, such as iron and aluminum oxides, are contained as complex silicates and various other compounds.

Table 1

Composition of Ores

Types of Ores	Constituents								
	U_3O_8	V_2O_5	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3	P_2O_5	CO_2
Uravan	0.15	1.9	87.0	1.12	0.85	0.89	3.24	0.09	0.80
Wild Steer Mine	0.35	3.4	86.6	1.01	0.45	1.04	3.3	0.12	0.55
Indian Reservation	1.6	2.0	87.0	1.16	0.41	2.64	2.6	0.25	0.17
Cactus Rat-Lot 134	0.16	1.4	87.4	1.6	0.65	1.76	2.3	0.27	0.56
Cactus Rat-Lot 254	0.14	0.50	88.1	1.05	0.86	1.73	3.5	0.30	0.41
Cactus Rat-Lot 411	0.095	1.4	86.5	2.2	0.4	1.6	3.6	0.25	1.19
Rifle	0.08	1.90	83.8	1.57	2.15	1.62	2.82	0.05	1.69
Rico	0.09	2.20	83.3	3.0	1.6	1.87	2.84	0.06	1.76
Mineral Mountain-683	0.21	1.55	81.5	3.97	1.52	1.46	3.84	0.11	2.47
Mineral Mountain-750	0.22	1.62	80.2	5.67	-	0.96	6.8	0.08	4.0

Some of the different batches of ore under investigation at Y-12 were selected in a manner such that they represent large deposits of ore which will be processed at some future time by the salt-roast, acid-leach (Rifle) method. For instance, the Uravan stockpile material is a composite sample representing a large quantity of ore which will be processed in the future at the Uravan site using the Rifle process. Other of the samples were selected because they are representative of true carnotite or roscoelite types and contain extraneous minerals, especially calcite, in various concentrations. The calcite concentration is an important consideration in the acid process, as will be shown by data in the following sections.

Each ore batch was prepared for laboratory investigations by first crushing all or most of the material to pass a 20 mesh sieve. Small representative samples of the crushed ore were then obtained by carefully riffling into quart jars. Sieve analyses, representative of the different batches of crushed ore are presented in Table 2.

It should be pointed out that the carnotite ores listed in Table 1 are by no means representative of all the different types of ores that are available in the Colorado region. For example, since the primary purpose of the work reported herein has been to investigate the salt-roast, acid-leach process, all of the ores tested contain fairly large amounts of V_2O_5. As will be seen below, the salt-roasting step in the process is designed entirely for vanadium recovery. Hence, it would be worthless to consider the handling of ores by this process that contain insufficient vanadium to pay for the roast operation.

Table 2

Sieve Analysis of Ores

Source	Mesh Identification	-20 + 40	-40 + 60	-60 + 80	-80 + 100	-100 + 140	-140 + 200	-200
Uravan	-20	15.2	26	20.4	13.5	13.5	5.4	6
Wild Steer	-20	11.7	31.8	18.2	10.0	12.6	6.5	9.2
Indian Reservation	-20	28	26	9.7	4.9	7	5.4	19
Cactus Rat-134	-18	23**	19	14.3	6.8	12.9	24	*
Cactus Rat-254	-18	26.7**	23	12.5	5.8	10.7	21.3	*
Cactus Rat-411	-18	30.6**	23	13.5	5.4	9.4	18.1	*
Rifle	-20	17.0	11.8	17.6	14.0	17.2	10.0	12.4
Rico	-20	13.6	10.6	8.4	18.6	30.6	8.2	10.0
Mineral Mountain 683	-20	12.7	14.9	11.7	11.3	22.9	9.7	16.7
Mineral Mountain 750	-20	15.8	19.4	13.4	10.8	18.7	7.8	14.1

* 200 screen not used on these runs.

** -18 + 40 Mesh instead of -20 + 40.

Other ores in the Colorado Plateau are mainly variant from those shown in that they are one or any combination of the following: higher in calcite content, much lower in uranium content, or much lower in vanadium content. In general, the acid-process is not suitable for application to these materials. Other processing methods either have been or will be developed.

PART I. A CRITICAL EXAMINATION OF THE SALT-ROAST - ACID LEACH PROCESS FOR WESTERN ORES

Introduction

The "acid-process" has been used for some time and is currently being used at the vanadium mill at Rifle, Colorado, owned and operated by the U. S. Vanadium Corporation. The same process is to be employed also in the U. S. Vanadium mill at Uravan, Colorado, at such time as that plant has been reconstructed and placed in operation.

Prior to the advent of the national demand for uranium, these mills operated only for the recovery of vanadium, and the process consisted simply of (1) a salt-roast, and (2) a water-leach to gain the soluble soda salt of vanadium. The uranium-bearing tailings were stockpiled for future reference. After uranium came into demand, these tailings were re-worked (acid-leached) for their uranium content. In addition, innovations were introduced into the mills so that the HCl was scrubbed from the roast gases and used to extract the uranium values.

The present process, as employed at Rifle, includes the steps listed below. In general, the ores handled at this plant are typical low lime, high vanadium carnotites or roscoelites. A flowsheet for the process is presented in Appendix B.

(1) The ore is crushed (dry) to less than 14 mesh, mixed with 8-10 percent of salt (NaCl) and roasted in a multiple-hearth furnace.

(2) Calcines from the roaster are first leached (percolation) with water which removes about 70-75 percent of the vanadium as water-soluble sodium vanadate.

(3) The water-leached tailings are then leached in place (percolation method) with dilute HCl solution which has been obtained by scrubbing out the HCl produced in the salt-roasting step. This operation removes over 90% of the uranium and also dissolves approximately 15% additional vanadium.

(4) The water leach is treated for vanadium recovery by precipitation as "red-cake". The acid leach is treated to obtain a concentrated precipitate of uranium and also a precipitate of iron vanadium which is recycled to the roasters.

A rather thorough examination has been made of the application of the acid process to a variety of ores, and the data from these studies are presented in the following sections. In gathering this information, four principal aspects of the process have been considered. These are: (1) factors affecting the recovery of uranium and vanadium, (2) the production of hydrochloric acid during roasting, (3) the consumption of

hydrochloric acid during leaching, and (4) the overall effect of CaO on the process. Solution Chemistry studies, for reasons discussed later, are not presented in this document.

From the results in general, it may be stated that, under optimum operating conditions and with certain types of ores, the acid process is efficient in the recovery of both uranium and vanadium. The major limitation of the process is imposed by the calcite concentration of the feed material.

Factors Influencing the Recoveries of Uranium and Vanadium by the Acid Process

Experimental Methods

Roasting tests were carried out by heating small quantities of the ore in a laboratory electric furnace fitted with an inlet for measured flow of air or other gases. One hundred gram batches of the ore (plus NaCl) were charged into the furnace in small platinum or porcelain boats. These boats were of such a size that the depths of the ore beds were either 1/4" or 1-1/4".

Two different methods for heating the ore were employed. In some cases, the ore was placed in the furnace at a temperature of 400°C., heated to the final roasting temperature over a period of about 20-30 minutes, and held at the final temperature for the desired length of time. These experiments are referred to in the discussion below as "heat-up" experiments. In other cases, the ore was charged directly into the furnace at the desired roasting temperature. These tests are referred

to as "constant temperature" experiments.

Water or acid leachings of raw ore or salt-roast calcines were carried out in 1-liter Berzelius beakers, agitation being supplied by motor-driven stirrers. Leach slurries were filtered on Buchner funnels and the ore residues were washed thoroughly in all cases with water (about 500 cc. per 100 gms. ore).

The acid liquors and ore tailings were analyzed for their uranium and vanadium contents. Percentage recoveries, as calculated for each experiment, were based on the total uranium or vanadium that was accounted for in the particular test; thus, nearly eliminating any variations due to sampling.

Influence of Roasting Temperature

Temperature is perhaps the most important single factor in the salt-roasting operation. Experimental results from the study of this variable are presented in Table 3.

In roasts of Uravan ore at different bed-depths (1/4" and 1-1/4") for various times, no reactions are apparent during treatments at 200°C. At a temperature of 600°C., only a small amount of vanadium has been changed to a water-soluble form although a large portion has been rendered soluble in acids. Considerable quantities of vanadium may be water-extracted, however, from ores roasted with salt at 750°C., and this quantity (for the roasting times indicated) increases to reach a maximum at a roasting temperature of about 850°C.

Table 3

Influence of Roasting Temperature

Exp. No.	Time (hrs.)	Temp. (°C.)	Bed-Depth (in.)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails: U % of Weight	Tails: U % of Total	Tails: V % of Weight	Tails: V % of Total
H-156	0.5	200	1/4	0.8	97	46	0.004	3	0.500	53
H-157	2.5	200	1/4	0.7	96	46	0.004	4	0.480	53
H-150	0.5	600	1/4	3	98	79	0.004	2	0.180	18
H-151	2.5	600	1/4	3	96	83	0.004	4	0.150	14
H-155	2.0	750	1/4	68	92	19	0.008	8	0.130	13
H-159	1.0	800	1/4	77	90	10	0.011	10	0.132	13
H-294	1.5	850	1/4	78	97	11	0.005	3	0.120	11
H-169	1.5	875	1/4	72	83	8	0.015	17	0.197	20
H-250	1.5	900	1/4	70	81	8	0.023	19	0.250	22
H-251	2.5	200	1-1/4	1	96	38	0.004	4	0.680	61
H-252	2.5	600	1-1/4	2	95	69	0.004	5	0.325	29
H-253	2.5	750	1-1/4	55	92	28	0.007	8	0.180	17
H-146	2.5	850	1-1/4	75	94	15	0.005	6	0.105	10
H-170	2.5	875	1-1/4	66	98	19	0.003	2	0.160	15
H-254	2.5	900	1-1/4	68	90	16	0.010	10	0.172	16

Roast Conditions: 100 gms. Uravan ore ground to minus 20 mesh roasted with 8% NaCl and a .24 cfm dry air flow over a 1/4" bed (heat-up) or a 1-1/4" bed (constant temperature).

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

With reasonable roasting times (as shown in Table 3), the uranium extractions are unaffected by a roasting temperature as high as 850°C., i.e., the uranium concentrations of the tailings are about the same as those from raw ore leachings (see Table 4, PART II). At higher roasting temperatures (875° to 900°C.), the extractions may or may not be affected, depending upon the bed-depth of the ore charge. For instance, from the results in Table 3, it is evident that considerable amounts of insoluble uranium are formed during salt-roasting of thin (1/4") ore beds at temperatures of 875-900°C. With similar roasting times and temperatures, this effect is not noticeable when roasting the salt-ore mix at bed-depths of 1-1/4".

Vanadium extractions are also affected by roasting at the higher temperatures. In general, a smaller portion of the vanadium is extracted by the water leach and a greater portion is left in the process tailings. As in the case of uranium, this effect is somewhat more pronounced with roasts of ore in thin beds.

It may be noted that the tests described thus far, have dealt entirely with Uravan ore. To show that similar temperature effects are observed during treatment of other materials, test results from roasts of certain other ores are presented in Table 4.

Though other roasting variables (time and bed-depth) must be considered in conjunction with the roasting temperature, it may be concluded from the data in general that 850°C. is about optimum for the salt-roasting step, from the standpoint of both uranium and vanadium recovery.

Table 4

Influence of Roasting Temperature

Exp. No.	Type of Ore	Temp. (°C.)	Extractions			Tails			
			H_2O Leach	Acid Leach					
			V	U	V	U		V	
			% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
H-191	Wild Steer	750	79	97	13	0.009	3	0.150	8
H-192	Wild Steer	850	85	97	9	0.009	3	0.127	6
H-193	Wild Steer	900	78	82	6	0.049	18	0.310	16
H-180	Indian Reservation	750	74	98	20	0.030	2	0.094	6
H-181	Indian Reservation	850	74	99	20	0.016	1	0.093	6
H-182	Indian Reservation	900	61	77	22	0.310	23	0.240	17
H-354	Rifle	850	86	98	6	0.001	2	0.090	8

Roast Conditions: 100 gms. of ore ground to minus 20 mesh roasted with 8% NaCl and a .24 cfm dry air flow over a 1/4" bed (Heat-up). Roast time = 1.5 hours.

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

The effects of bed-depth and time are discussed immediately below.

Influence of Roasting Time

As shown by the data in Table 5, the role of time in the roasting operation is directly dependent upon the roasting temperature and bed-depth of the charge. At any given bed-depth and roasting temperature (above that necessary to initiate the "roast reactions"), the extraction of vanadium by the water leach increases to a maximum with increasing time for the roast. For instance, with 1/4" beds of Uravan ore, a maximum extraction of about 80% of the vanadium may be obtained in the water leach after roasting for one hour at 850°C. To attain this same extraction by an 800°C. roast, the time of treatment must be extended to 2 hours, and at 750°C., to about 3 hours. In deeper bed roasts, comparatively longer times are required to obtain optimum vanadium extractions under comparable temperature conditions. For example, as also shown by the data in Table 5 for Uravan and other ores, several hours are necessary to yield maximum vanadium extractions at a roasting temperature of 850°C. and a bed-depth of 1-1/4".

Excessive roasting times (at 850°C.or above) have much the same deleterious effect on uranium extractions as excessive temperatures. When the two are acting in combination, the effects are additive. In thin (1/4") bed roasts at 850°C., for example, the uranium extraction drops from 97 to 75% by increasing the roasting time from 1.5 to 3 hours. At 875°C., the uranium is 94% soluble after 1 hour and 83% soluble after 1.5 hours; and at 900°C., only 49% of the uranium is soluble after 2 hours

Table 5

Influence of Roasting Time

Exp. No.	Time (hrs.)	Temp. (°C.)	Bed Depth (in.)	Source of Ore	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
H-154	1.0	750	1/4	Uravan	57	93	31	0.008	7	0.120	12
H-155	2.0	750	1/4	Uravan	68	92	19	0.008	8	0.130	13
H-134	3.0	750	1/4	Uravan	78	92	11	0.008	8	0.110	11
H-158	0.5	800	1/4	Uravan	71	94	14	0.006	6	0.170	15
H-159	1.0	800	1/4	Uravan	77	90	10	0.010	10	0.132	13
H-160	2.0	800	1/4	Uravan	80	92	7	0.008	8	0.132	13
H-255	0.0	850	1/4	Uravan	49	91	31	0.009	9	0.225	20
H-256	0.5	850	1/4	Uravan	66	94	19	0.007	6	0.168	15
H-257	1.0	850	1/4	Uravan	82	94	2	0.007	6	0.161	16
H-294	1.5	850	1/4	Uravan	78	97	11	0.005	3	0.122	11
H-278	2.0	850	1/4	Uravan	80	95	7	0.006	5	0.138	13
H-279	2.5	850	1/4	Uravan	80	87	7	0.017	13	0.135	13
H-295	3.0	850	1/4	Uravan	78	75	7	0.040	25	0.166	15
H-298	1.0	875	1/4	Uravan	73	94	12	0.009	6	0.164	15
H-169	1.5	875	1/4	Uravan	72	83	8	0.015	17	0.196	20
H-301	1.0	900	1/4	Uravan	64	74	11	0.043	26	0.250	25
H-250	1.5	900	1/4	Uravan	70	81	8	0.023	19	0.250	22
H-302	2.0	900	1/4	Uravan	60	49	8	0.075	51	0.320	32
H-146	2.5	850	1-1/4	Uravan	75	94	15	0.005	6	0.105	10
H-280	6.0	850	1-1/4	Uravan	79	98	13	0.003	2	0.090	8
H-450	2.0	900	1-1/4	Uravan	75	94	14	0.009	6	0.116	11
H-451	4.0	900	1-1/4	Uravan	73	72	8	0.039	28	0.210	19

Table 5

Influence of Roasting Time

Exp. No.	Time (hrs.)	Temp. (°C.)	Bed Depth (in.)	Source of Ore	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails: U % of Wt.	Tails: U % of Total	Tails: V % of Wt.	Tails: V % of Total
H-175	1.0	850	1-1/4	Indian Reservation	52	99	41	0.013	1	0.097	7
H-176	2.5	850	1-1/4	Indian Reservation	67	99	27	0.011	1	0.079	6
H-177	4.0	850	1-1/4	Indian Reservation	68	99	27	0.009	1	0.076	5
H-193	1.0	850	1-1/4	Wild Steer	67	96	25	0.010	4	0.144	8
H-194	2.5	850	1-1/4	Wild Steer	81	96	13	0.010	4	0.120	6
H-195	4.0	850	1-1/4	Wild Steer	83	97	11	0.009	3	0.105	6

Roast Conditions: 100 gms. ore ground to minus 20 mesh roasted with 8% NaCl and a .24 cfm dry air flow over a 1/4" bed (heat-up) or a 1-1/4" bed (constant temperature).

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

of roasting.

Vanadium extractions are also reduced by heating thin ore beds for extended times at high temperatures. At 900°C., for instance, 22% of the vanadium is retained by the tailings after a 1.5 hour roast and 30% after a 2 hour roast.

With deep (1-1/4") beds, the effect of roasting time is less severe. At 900°C., recoveries are decreased after 4 hours of roasting but are not noticeably affected after 2 hours.

Since the time and temperature effects are so interdependent, it is suggested that Tables 3, 4, and 5 be reviewed in combination. From these data, it may be concluded that the optimum roasting time is about 1-1/2 hours at a temperature of 850°C. for thin ore beds. A discussion of the bed-depth effect versus plant operation is presented in a later section.

Effect of Moisture in Roast Atmosphere

Water vapor is present during plant roasting operations due to the combustion of the fuel (coal) in the multiple-hearth roasters. As will be discussed later, the presence of some moisture is required during the roast for the production of maximum amounts of HCl, though increasing the concentration above a certain level is of little further advantage (see page 59). However, during roasting of thin (1/4") beds of salt-ore mixtures at 850-900°C., the presence of moisture above a certain level affects the subsequent recovery operation in that decreasing amounts of uranium (and to a lesser extent, vanadium) are leached from the ore with the presence of increasing quantities of the water vapor. In roasts

of ores in deeper beds or at lower temperatures, this effect is not demonstrated.

It may be noted from Table 6 that a contact of 12 gms. of water with 100 gms. of ore in a 1/4" bed (850°C.) gave a small but significant decrease in uranium extraction whereas the same quantity of water in contact with a 1-1/4" bed produced no effect. Larger amounts of water (e.g., 55 gms. H_2O/100 gms. ore) reduced the soluble uranium from 95 to 49% and and the soluble vanadium from 86 to 76%. Again this effect was not demonstrated with deeper bed depths or a lower (750°C.) roasting temperature.

Fortunately, the calculated quantity of water which contacts the ore in a plant multiple-hearth roaster is in the order of 8-10 gms. of H_2O for each 100 gms. of ore (an amount just below the critical point for thin beds as shown in Table 6). If for some reason, the moisture is increased (as, for instance, to gain a small increase in HCl production), the "effective" bed-depth of the plant roaster must be understood before the laboratory data could be translated to a plant scale. A comparison of laboratory and plant bed-depths is presented in a subsequent section.

The reason for the adverse effect of moisture during salt-roasting of thin ore beds (but not deep) is not completely understood. Experiments made with process tailings (see page 43) suggest that this might be due to the action of water as an aid in forming complex, insoluble uranium compounds (perhaps complex silicates). Also, since moisture has little effect on the recovery of the values when present during the roasting of

Table 6

Influence of Moisture in Roast Atmosphere

Exp. No.	Time (hrs.)	Bed Depth (in.)	Moisture (gms.)	Temp. (°C.)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
H-247	1.5	1/4	2-5	850	76	95	10	0.006	5	0.152	14
H-225	1.5	1/4	12	850	78	86	6	0.017	14	0.186	16
H-226	1.5	1/4	26	850	74	74	8	0.034	26	0.210	18
H-224	1.5	1/4	55	850	70	49	6	0.072	51	0.270	24
H-229	2.5	1-1/4	22	850	76	95	12	0.006	5	0.138	12
H-230	2.5	1-1/4	66	850	78	91	9	0.012	9	0.150	13
H-161	1.5	1/4	90	750	65	92	23	0.010	8	0.116	12
H-162	1.5	1/4	75	800	73	75	12	0.026	25	0.142	15
H-163	1.5	1/4	70	850	64	19	6	0.075	81	0.300	30
H-164	1.5	1/4	80	900	51	16	6	0.072	84	0.430	43
H-138	2.5	1-1/4	90	875	82	95	8	0.005	5	0.090	10
H-139	2.5	1-1/4	90	875	80	94	10	0.006	6	0.105	10

Roast Conditions: 1. 100 gms. Uravan ore ground to minus 20 mesh roasted with 8% NaCl in a 1/4" bed (heat-up) or a 1-1/4" bed (constant temperature), .24 cfm air(+moisture) was passed over the charge.

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

ores in deeper beds (1-1/4"), it is indicated that this effect may be due to some more indirect mechanism involving reactions of the Cl_2 or HCl produced by the salt roast (these gases being rapidly dispersed from the thin beds but remaining in good contact for longer periods with the deep beds).

For instance, in a thin bed test (H-163), a contact of 70 gms. of moisture with 100 gms. of ore caused 81% of the uranium to be retained in the tailings. In a deep bed test (H-118) at about the same temperature and moisture concentration, only 5% of the uranium was retained in the tailings even though about 1/3 of the total ore (due to the shape of the containers) was in the upper 1/4" layer. The obvious difference between the two tests is that the gases produced in the roast are speedily liberated from the thin beds whereas they are more slowly supplied over longer periods from the bottom layer in the deeper beds.

To test the theory concerning the roast gas effect, tests will be made later in which thin beds of ore are treated with varying mixtures of gaseous H_2O, HCl, and air.

Influence of Ore Bed-Depth

The influence of bed-depth on the laboratory salt-roasting experiments has been described rather fully during previous discussions concerning the effects of temperature, time, and moisture content of the roast atmosphere. A compositing of some of the data, which show further that the roasting conditions are less critical with deeper ore beds, are presented in Table 7.

Table 7

Influence of Ore Bed-Depth

Exp. No.	Time (hrs.)	Bed Depth (in.)	Temp. (°C.)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails: U % of Wt.	Tails: U % of Total	Tails: V % of Wt.	Tails: V % of Total
H-147	2.5	1/4	850	80	82	6	0.017	18	0.145	14
H-146	2.5	1-1/4	850	75	94	15	0.005	6	0.105	10
H-280	6.0	1-1/4	850	79	98	13	0.003	2	0.090	8
H-165	2.5	2	850	76	95	16	0.005	5	0.086	8
H-143	1.5	1/4	875	74	69	5	0.032	31	0.220	21
H-142	1.5	1-1/4	875	72	96	15	0.004	4	0.125	13
H-169	1.5	1/4	875	70	72	10	0.029	28	0.197	20
H-170	1.5	1-1/4	875	66	98	19	0.003	2	0.161	15
H-145*	2.5	1/4	875	63	41	5	0.058	59	0.330	32
H-144*	2.5	1-1/4	875	75	86	7	0.014	14	0.195	18
H-301	1.0	1/4	900	64	74	11	0.044	26	0.250	25
H-302	2.0	1/4	900	60	49	8	0.075	51	0.320	32
H-254	2.5	1-1/4	900	68	90	16	0.009	10	0.173	16

Roast Conditions: 100 gms. Uravan ore ground to minus 20 mesh roasted with 8% NaCl and a .24 cfm dry air flow over a 1/4" bed (heat-up) or a 1-1/4" (or 2") bed (constant temperature).

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

* No air flow during roast.

A direct translation of laboratory data to plant operation is difficult due to the physical differences in the roasting processes. The small laboratory tests were necessarily made with static beds, varying in depth from 1/4" to 1-1/4". In the plant, multiple-hearth roaster, the bed-depth in each hearth is about 4" but the ore is continuously rabbled to increase the surface exposure.

In the few cases where it is possible to draw some comparison between laboratory and plant data, it is found that the 1/4" experimental roasts are very similar to plant roasts from the standpoint of the proportions of vanadium and uranium that are extracted by the various leaches and also from the standpoint of HCl production during the salt-roasting step. In other words, the gas-ore contact in the 1/4" static bed is about the same as obtained with thicker, rabbled beds in the plant.

It does not necessarily follow that the same criticality of conditions that exist for the thin static beds will also be applicable to the hearth roasting. It has been pointed out in previous sections that deep beds may be less susceptible to certain variables (high temperature, long times, and high moisture content) because of the longer contact with gases produced in the roast. If this is the case, the plant operation should have some of the characteristics of a deep, static-bed roast in that the roast produced gases are in continuous contact with the ore in the multiple-hearth.

It may be concluded with confidence, of course, that the conditions which satisfy the thin bed roasts will also give good operating

results in the plant. Tests, on a plant scale of operation, would be required to accurately determine whether these conditions could be applied with fewer restrictions.

Influence of Air in Roast Atmosphere

The uranium and vanadium recoveries obtained by roasting various ore batches with or without air (nitrogen atmosphere) are presented in Table 8. The formation of water soluble vanadium was low, in the absence of air, for all the ores, but a large portion was converted to an acid soluble form, and the total extractions were well in the range of those obtained from standard roasts. Uravan ore was apparently least affected with a conversion of 57 percent into the H_2O soluble form (standard 70-75%), and Wild Steer the most affected with a conversion of only 27% (standard 80%). Indian Reservation and Cactus Rat fell in between with conversion of 50% (standard 70%) and 42% (standard 72%), respectively. The uranium recoveries from all of the ores tested were normal.

It is evident then that the presence of air during the roast is very instrumental to the conversion of vanadium into the water soluble form, but has little effect on the recoverable uranium. This is undoubtedly due to the fact that vanadium exists to a certain extent in the ores as a reduced form, and the higher oxidation stage (+5) must be obtained in the roast in order to form the water-soluble sodium vanadate. Only a small flow of air through the furnace is required to satisfy this reaction during the normal roasting time cycle.

The variations in water-soluble vanadium from different ores

Table 8

Influence of Air in Roast Atmosphere

Exp. No.	Furnace Atmosphere	Source of Ore	Extractions			Tails			
			H_2O Leach	Acid Leach					
			V	U	V	U		V	
			% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
H-265	dry air	Uravan	67	92	15	0.010	8	0.195	18
H-261	dry N_2	Uravan	57	92	28	0.009	8	0.170	15
H-192	dry air	Wild Steer	85	97	9	0.009	3	0.127	6
H-262	dry N_2	Wild Steer	27	91	64	0.022	9	0.175	9
H-181	dry air	Indian Reservation	74	99	20	0.016	1	0.093	6
H-263	dry N_2	Indian Reservation	50	98	42	0.016	2	0.100	8
H-198	dry air	Cactus Rat-Lot 134	72	94	13	0.009	6	0.121	15
H-264	dry N_2	Cactus Rat-Lot 134	42	94	35	0.009	6	0.160	23

Roast Conditions: 100 gms. ore ground to minus 20 mesh roasted with 8% NaCl at 850°C. for 1-1/2 hrs. and a gas flow of .24 cfm over a 1/4" bed (heat-up).

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

(after a N_2 roast) may be attributed to their differences in oxidized (+5) vanadium content.

Effect of CO_2 and SO_2 in Roast Atmosphere

Since the multiple-hearth roasters are coal fired, rather copious quantities of CO_2 are present during plant roasts. Fortunately, this gas has no effect on the recovery of either vanadium or uranium, even at concentrations up to ten times those normally incurred in plant operation (see Table 9).

Sulfur dioxide is also produced in the multiple-hearth roaster from the oxidation of pyrite in the coal. Although this compound has some effect on the formation of HCl during roasting (see section on HCl production), no observable effect on the uranium and vanadium extractions is demonstrated by the presence of ten times the normal plant quantities (Table 9).

It is indicated by experiment H-216 that the presence of SO_2 will somewhat inhibit the deleterious effect of moisture. However, since the data is meager, and since the moisture concentration in this experiment was in the critical range, general conclusions cannot be drawn.

Effect of NaCl Concentration

Within fairly wide limits of variation (see Table 10), the NaCl concentration during the roast has little effect on subsequent recovery operations. The minimum amount of NaCl required for maximum conversion of vanadium to water-soluble sodium vanadate will vary from ore to ore

Table 9

Influence of CO_2 and SO_2 in Roast Atmosphere

Exp. No.	Time (hrs.)	Special* Treatment during Roasting (gms. gas per 100 gms. ore)	Moisture (gms. per 100 gms. ore)	Bed Depth (in.)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails: U % of Wt.	Tails: U % of Total	Tails: V % of Wt.	Tails: V % of Total
H-227	1.5	47 g. CO_2	none	1/4	77	95	8	0.007	5	0.154	15
H-228	1.5	470 g. CO_2	none	1/4	76	95	9	0.006	5	0.153	15
H-210	1.5	1.0 g. SO_2	none	1/4	77	93	10	0.008	7	0.153	13
H-211	1.5	40.0 g. SO_2	none	1/4	75	92	11	0.009	8	0.155	14
H-212	2.5	1.0 g. SO_2	none	1-1/4	81	95	3	0.007	5	0.142	16
H-213	2.5	32.5 g. SO_2	none	1-1/4	73	90	16	0.013	10	0.134	11
H-215	1.5	0.5 g. SO_2	15	1/4	76	94	9	0.007	6	0.163	15
H-214	2.5	0.5 g. SO_2	18	1-1/4	72	95	16	0.006	5	0.130	12

Roast Conditions: 100 gms. Uravan ore ground to minus 20 mesh roasted with 8% NaCl at 850°C. and a gas (plus air) flow of .24 cfm over a 1/4" bed (heat-up) or 1-1/4" bed (constant temperature).

H_2O Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

* It has been estimated that 0.2 gm. SO_2 per 100 gms. ore and 40 gms. CO_2 per 100 gms. ore pass through the roaster in actual plant conditions.

Table 10

Influence of NaCl Concentration

Run No.	Time (hrs.)	NaCl (%)	Type of Ore	Bed Depth (in.)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
H-259	1.5	0	Uravan	1/4	6	86	35	0.015	14	0.695	59
H-234	1.5	3	Uravan	1/4	65	90	18	0.011	10	0.196	17
H-235	1.5	6	Uravan	1/4	75	93	11	0.008	7	0.160	14
H-236	1.5	9	Uravan	1/4	75	95	11	0.007	5	0.151	14
H-237	1.5	12	Uravan	1/4	76	96	11	0.006	4	0.143	13
H-238	1.5	15	Uravan	1/4	74	95	13	0.007	5	0.144	13
H-239	1.5	18	Uravan	1/4	65	95	21	0.006	5	0.139	14
H-260	2.5	0	Uravan	1-1/4	6	88	38	0.015	12	0.640	56
H-242	2.5	12	Uravan	1-1/4	68	95	19	0.005	5	0.140	13
H-243	2.5	15	Uravan	1-1/4	70	95	18	0.006	5	0.135	12
H-172	2.5	8	Indian Reservation	1-1/4	67	99	27	0.011	1	0.084	6
H-174	2.5	10	Indian Reservation	1-1/4	71	99	24	0.011	1	0.076	5
H-179	2.5	12	Indian Reservation	1-1/4	66	99	28	0.009	1	0.081	6
H-185	2.5	8	Wild Steer	1-1/4	82	96	14	0.011	4	0.104	4
H-186	2.5	10	Wild Steer	1-1/4	80	97	13	0.008	3	0.118	7
H-187	2.5	12	Wild Steer	1-1/4	81	97	14	0.008	3	0.090	5

Roast Conditions: 100 g. ore ground to minus 20 mesh roasted at 850°C. and a dry air flow of .24 cfm over a 1/4" bed (heat-up) or a 1-1/4" bed (constant temperature)

H_2O Leach Conditions: 200 ml. H_2O per 100 g. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 g. ore for 2 hours at 80°C.

depending upon the quantity of vanadium present. For Uravan ore, 6-8% NaCl is sufficient for maximum conversion at a roasting temperature of 850°C. and a roasting time of 1-1/2 hours. Since the other ores studied are fairly similar to Uravan ore in vanadium content, the same quantity of salt is also sufficient for the treatment of these materials.

The use of rather large quantities of salt in the salt-roasting step has little apparent effect on the subsequent recoveries of uranium or vanadium. With Uravan ore, a concentration of 8% NaCl represents about a 7-fold excess for conversion of all of the vanadium in the ore to sodium meta-vanadate. Identical recoveries of uranium and vanadium were obtained when using a 21-fold excess (18% NaCl). It is known that too much NaCl in the plant reactor causes mechanical difficulties due to slagging. Apparently this factor, rather than any chemical reactions, imposes the upper limit of allowable salt concentration.

By certain experiments in Table 10, it is shown that roasting of the ores in a complete absence of salt causes a small but significant decrease in the uranium extractions (vanadium extractions are obviously low since sodium is not supplied for the formation of sodium vanadate). Apparently some small tendency of the uranium to react during the roast to form insoluble compounds (e.g., silicates) is offset by the presence of the sodium chloride.

Effect of Iron Vanadate Recycle

As shown by previous descriptions of the acid (Rifle) process, about 10-15% of the total vanadium in the head ore is obtained in the acid

leach solution, and this material is precipitated as iron vanadate and returned to the roaster. To determine whether this recycle has any effect on recoveries of uranium and vanadium, experiments were conducted as follows:

Iron vanadate was added to Uravan ore in such quantities as to double or triple the original vanadium content and these mixtures were roasted under "normal" conditions, i.e., 1.5 hours at 850°C. (heat-up) with a .24 CFM air flow over a 1/4" bed. The NaCl concentration was increased from 8% (normal) to 10% and 12%, respectively, for the double and triple vanadium roasts so as to assure a sufficient amount of salt for complete reaction. It is known from previous work that a NaCl concentration within this range (8-12%) produces no noticeable effect on uranium or vanadium extraction; hence, it may be assumed that this variation of the salt concentration does not produce another variable in these tests. The ferric vanadate was prepared by adding ferric nitrate to an aqueous solution of sodium meta-vanadate.

It may be noted from the results in Table 11 that the recovery of uranium was apparently unaffected by doubling or even tripling the vanadium content as iron vanadate; the recoveries obtained by a "normal" run being well in agreement with those in which the vanadate was added

The recycled iron vanadate also showed no effect on the vanadium extraction, as demonstrated by the constant amount of vanadium left in the tailings from the three experiments. Essentially all of the recycled vanadium is apparently re-extracted after the roasting treatment.

Table 11

Influence of Recycled Iron Vanadate

Exp. No.	NaCl (%)	V Added as Iron Vanadate (mg.)	Extractions			Tails			
			H_2O Leach	Acid Leach		U		V	
			V	U	V				
			% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
H-236	8	0	75	95	11	0.006	5	0.151	14
H-290	10	1080	87	96	6	0.006	4	0.160	7
H-289	12	2160	86	96	10	0.005	4	0.145	4

Roast Conditions: 100 g. Uravan ore ground to minus 20 mesh roasted at 850°C. for 1.5 hours, with a .24 cfm dry air flow over a 1/4" bed (heat-up). The vanadium in H-290 and H-289 represents a 2 and 3-fold increase (respectively) of the original concentration.

Water Leach Conditions: 200 ml. H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 gms. ore for 2 hours at 80°C.

Effect of Calcite Content of the Ore

A large number of the Western ores are high in calcite content. These deposits have been ignored in past mining of the region since it was known that large quantities of calcite had certain deleterious effects on the recovery operation. However, a determination had never been made of the limiting amount of calcite that could be tolerated by the acid process.

During the early part of the program at Y-12, when only a few samples of ore were available, roasting tests were made on high-lime ores which were "synthesized" by adding $CaCO_3$ to a low-lime sample. As more ore samples of varied calcite content were received, the roasting experiments were re-run on these materials. Data from the two types of experiments are presented in Table 12, and the results are in fair agreement.

The uranium recoveries from high lime ores were not much different than those from low lime ores. The overall extractions of vanadium were also good. However, with increasing contents of CaO in the ores, decreasing amounts of vanadium were extracted by the water leach, and increasing amounts were extracted by the acid leach. This phenomenon is undoubtedly caused by the formation in the roast of increasing amounts of water-insoluble, acid-soluble calcium vanadate, rather than the water-soluble sodium vanadate.

With ores containing calcite in concentrations greater than 5% as CaO, almost no water-soluble vanadium was formed by the roast. Also, the acid leach slurries of the high lime calcines were difficult to filter because large amounts of acid-soluble silicates were formed during

Table 12

Influence of Calcite Content of the Ore

Exp. No.	Source of Ore	CaO (%)	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
H-294	Uravan	1.12	78	97	11	0.005	3	0.120	11
H-271	Uravan (+ $CaCO_3$)	3	39	92	46	0.010	8	0.150	15
H-272	Uravan (+ $CaCO_3$)	4	16	90	72	0.012	10	0.128	12
H-273	Uravan (+ $CaCO_3$)	5	9	90	79	0.012	10	0.126	12
H-274	Uravan (+ $CaCO_3$)	7	1	94	84	0.009	6	0.158	15
H-316	Rifle	1.6	85	95	5	0.002	5	0.100	10
H-201	Cactus Rat-Lot 411	2.2	58	90	26	0.008	10	0.122	16
H-315	Rico	3.0	48	86	44	0.009	14	0.092	8
H-311	Mineral Mountain-683	4.0	52	89	34	0.016	11	0.125	14
H-313	Mineral Mountain-750	5.7	1.5	91	88*	0.013	9	0.090	10

Roast Conditions: 100 gms. ore ground to minus 20 mesh roasted with 8% NaCl for 1.5 hours at 850°C. and a .24 cfm dry air flow over a 1/4" bed (heat-up). The calcium was added to the Uravan ore in the form of $CaCO_3$.

H_2O Leach Conditions: 200 ml. of H_2O per 100 gms. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. of 5% HCl per 100 gms. ore for 2 hours at 80°C.

* Two acid (5%) leaches were necessary for normal vanadium extraction.

the roast and silica gels were deposited from the leach liquors.

The separation of a fair percentage of quite pure vanadium from the roasted ore by water-leaching is an essential part of the acid process. For satisfactory operation of this process, it is obvious that the calcite content of the head ore must be restricted. From the results as given in Table 12, this restriction would mean a calcite content in the head ores of less than 2.5% as CaO.

Other limitations on the calcite concentration in the ores are imposed by the effect which this material demonstrates on the production of HCl during roasting and the consumption of HCl during leaching. Discussion of these effects, as well as a summary of the overall effect of calcite on the acid process, are presented in later sections of this report.

Influence of Other Constituents of the Ore

Since the main constituents of carnotite ores, excluding silica and calcium, are iron, aluminum, and magnesium, it was considered important to determine what effect certain compounds of these elements might have on the acid process. Accordingly, a number of roasting experiments were performed in which known quantities of Fe_2O_3, Al_2O_3, MgO, and $AlPO_4$ had been intimately mixed with the salt-ore charge.

None of the compounds tested produced deleterious effects by decreasing either the percentage of uranium or vanadium extracted from the ore (Table 13). Discussions as to the effects of these compounds on HCl production and consumption are presented in a later section.

Table 13

Influence of Other Constituents of the Ore

Exp. No.	Total Concentration of Impurities* (%)	Extractions			Tails			
		H_2O Leach	Acid Leach					
		V	U	V	U		V	
		% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
H-282	1.78% Fe_2O_3	74	93	12	0.009	7	0.150	14
H-283	6.48% Al_2O_3	69	93	15	0.009	7	0.150	16
H-284	3.44% Al as $AlPO_4$	60	96	26	0.006	4	0.150	14
H-285	1.70% MgO	75	95	12	0.007	5	0.130	13
H-286	3.4% MgO	77	95	11	0.007	5	0.130	12

Roast Conditions: 100 g. Uravan ore ground to minus 20 mesh roasted with 8% NaCl for 1.5 hours at 850°C. and a dry air flow of .24 cfm over a 1/4" bed (heat-up). The Mg was added in the form of $MgCO_3$.

H_2O Leach Conditions: 200 ml. H_2O per 100 g. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 g. ore for 2 hours at 80°C.

* Original concentration of the impurities in the ore are given in Table , page .

It was interesting to note that with double or even triple the original concentrations of MgO in the ore, the formation of water-soluble vanadium was not affected, whereas, with similar concentrations of CaO, the water-soluble vanadium was reduced considerably. The effect of CaO is attributed to the formation of a water-insoluble calcium vanadate. Apparently, a like compound of magnesium is either not formed during the roast or is dissolved by the water leach.

Influence of Ore Mesh Size

To obtain some information as to the effect of ore particle size on the roasting operation, a batch of process tailings was separated into various size fractions and each fraction was analyzed for its uranium and vanadium content. The results from these experiments are presented in Table 14 below.

As shown by the comparatively high vanadium content of the 20-40 mesh fraction, a particle size below about 40 mesh is optimum for the roast from the standpoint of vanadium recovery. Somewhat higher vanadium concentrations are again realized in the very fine fractions. This may be expected since the formation of insoluble compounds should be predominant in the sample containing the largest amounts of reactive bases.

The uranium concentrations of the calcines as a function of particle size were reasonably constant except for a small increase in the fine fractions.

In plant practice, the ore is ground to pass a 14 mesh screen with most of the ore passing 40 mesh. Since grinding costs increase with

decreasing mesh size, it appears that a minus 14 mesh grind is at least close to optimum for plant scale operations.

Table 14

Uranium and Vanadium in Calcines of Different Mesh Size

Sample Description (U. S. Sieve No.)	Percent of Total Calcine Weight	Analysis U(%)	Analysis V(%)
Original tailing	-	0.023	0.18
		0.023	0.20
-20 and +40 mesh fraction	3.6	0.020	0.43
		0.020	0.42
-40 and +60 mesh fraction	18.0	0.020	0.14
		0.018	0.14
-60 and +80 mesh fraction	20.3	0.027	0.10
		0.027	0.09
-80 and +100 mesh fraction	15.5	0.026	0.11
		0.027	0.11
-100 and +140 mesh fraction	21.0	0.013	0.17
		0.012	0.16
-140 and +200 mesh fraction	9.6	0.033	0.22
		0.035	0.20
-200 mesh fraction	12.0	0.029	0.34
		0.029	0.35

Origin of Tailing Sample Used Above - To accentuate differences in sample analyses, the tailing was prepared, purposely, to contain higher than normal quantities of uranium and vanadium. Two-hundred grams of Uravan ore was roasted at 850°C. in a 1/4" bed for 1-1/2 hours and in the presence of water vapor (30 g. contact). Soluble values were removed by leaching once with water and twice with 10 percent HCl solution.

Influence of Calcine Aging

To determine whether the aging time of the salt roasted calcines had any effect on the subsequent extractions of uranium and vanadium, experiments were conducted in the following manner: Two 100-gm. samples of Uravan ore were salt roasted under identical conditions. After roasting, the two charges were mixed and re-separated by riffling into two identical samples so as to eliminate any variations in the roast procedure. Samples were aged for various lengths of time before processing through the water-leach, acid-leach cycle.

From the data as presented in Table 15, it may be concluded that the aging time of the salt-roasted calcines has no effect on the subsequent recoveries of uranium and vanadium by leaching.

Table 15

Effect of Aging

Mixture No.	Aging Time (hrs.)	Extractions			Tails			
		H_2O Leach	Acid Leach					
		V	U	V	U		V	
		% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
H-148-149	0	79	90	6	0.010	10	0.150	15
H-149-149	24	81	91	7	0.011	9	0.125	11
H-152-153	24	80	94	9	0.007	6	0.110	11
H-152-153	48	79	94	9	0.007	6	0.120	12

Procedure: 1. 100 gms. Uravan ore ground to minus 20 mesh containing 8% NaCl.

2. Samples were given a heat-up period (400-850°C.) and held for 1-1/2 hours at 850°C. in a .24 CFM dry air stream. Sample bed-depth was 1/4".

3. Aging times were measured from the time at which the calcines reached 60°C. by air cooling (about 15 minutes).

Studies of Process Tailings

By data presented above, it has been shown that upon roasting the salt-ore mix according to certain conditions, e.g., at high temperature or in the presence of water vapor, considerable quantities of uranium (and to a lesser extent, vanadium) are retained by the leached calcines. To derive some information as to the nature of this "hold-up", samples of highly contaminated calcines were subjected to the various tests described below in Table 16.

Table 16

Tests of Process Tailings

Description of Sample	Analysis of Sample U (%)	Analysis of Sample V (%)
Original tailing obtained by treating Uravan ore according to the procedure described below.	0.035 0.034	0.28 0.28
Sample obtained by treating 50 g. of original tailing with 100 ml. of 20% HNO_3 for 2 hours at 80°C.	0.033 0.032	0.22 0.27
Sample obtained by grinding 50 g. of original tailing to -100 mesh and treating with 100 ml. of 20% HNO_3 for 2 hours at 80°C.	0.031 0.029	0.25 0.26
Sample obtained by grinding 50 g. of original tailing to -100 mesh and treating with 100 ml. of 50% HCl for 2 hours at 80°C.	0.023 0.021	0.24 0.26
Sample obtained by treating original tailing with 1:1 HF for 15 minutes at room temperature	0.004 0.004	0.04 0.04

Origin of Tailing Sample - The calcine used for the experiment outlined above was obtained by roasting 200 g. of -20 mesh Uravan ore with 8% NaCl for 1-1/2 hours at 900°C. (1/4" bed-depth). The roasted product was leached once with water and twice with 10% HCl.

Prior to this work it was considered that the retention of uranium (and vanadium) might be due to either the physical hold-up by slagging or to the formation of insoluble compounds (perhaps complex silicates). However, as shown by Table 16, thorough crushing of the calcined particles failed to increase the vanadium or uranium extraction. This fact, combined with the high solubilities in hydrofhloric acid, suggests the latter of the above reasons to be the most probable.

Volatilization of Compounds during the Roast

The volatilization of various metallic compounds during the roasting treatment has been estimated by various persons as being very slight. However, no actual data are immediately available on this point. It was considered worthwhile to obtain some information on this matter, even though it is of no particular importance to plants in which the off-gases are scrubbed for HCl.

Uravan ore (540 gm.) with 9% NaCl was roasted in 130 gm. batches in a quartz tube furnace. The air flow was held at a low value to avoid dusting and the ore was roasted at 850°C. for 90 minutes. The sublimate which formed on the walls of the reactor tube and the exit tube was removed by a water wash followed by a dilute nitric acid wash. Practically all of the material was solubilized by the water wash. This solution was analyzed for uranium, vanadium, iron, aluminum, magnesium, calcium, and silica. The resulting date are presented in Table 17.

It is apparent that only small quantities of metallic compounds are volatilized during roasting. About 0.14 g. of uranium and 4.0 mg. of

vanadium were volatilized per 100 gm. of Uravan ore. This corresponds to about 0.1% of the uranium and 0.4% of the vanadium value in the head sample. These quantities are probably negligible compared with the dusting which occurs in plant operations.

Table 17

Metals Volatilized during the Roasting Treatment

Constituent	mg. Volatilized per 100 gm. ore	Percent of Head Content Volatilized
Uranium	0.14	0.1
Vanadium	4.0	0.4
Iron	3.0	0.5
Magnesium	2.0	0.4
Calcium	2.0	0.2
Silica	2.0	0.002
Aluminum	1.0	0.06

Procedure: 540 gm. of Uravan ore roasted in about 130 gm. batches in a tube furnace at 850°C. for 90 minutes. Air flow held at 0.1 cu. ft./minute. Sublimate on walls of tube dissolved in dilute HNO_3.

Water Leaching of the Calcines

Rate of Vanadium Dissolution by the Water Leach - The rate of vanadium (sodium vanadate) dissolution by the water leach solution has been studied in the following manner: Two-hundred grams of calcined ore was agitated with 400 ml. of water in a constant temperature bath at

80°C. (water preheated to 80°C. before mixing). Samples of the ore were "thiefed" from the mixture at various time intervals and were quickly filtered and washed on a large Buchner funnel (time for this operation equaled about one minute). Duplicate determinations for vanadium were obtained on each sample.

Results from these experiments are presented in Table 18. Apparently the extraction of water soluble vanadium at 80°C. is virtually complete after a contact period of 10 minutes.

Rate studies of water leaching at room temperature have not been made. From a few miscellaneous experiments, it is known, however, that thorough dissolution of the water soluble vanadium can be attained at this temperature.

Table 18

Rate of Vanadium Extraction in H_2O Leach

Experiment No.	Time of Contact (minutes)	Analysis of Tails % V		% V_2O_5
L-369A	5	0.29,	0.29	0.54
L-369B	10	0.24,	0.25	0.47
L-369C	20	0.26,	0.25	0.48
L-369D	30	0.23,	0.25	0.45
L-369E	90	0.25,	0.26	0.48
L-369F	240	0.25,	0.23	0.45

1. Roast: -20 mesh Uravan ore, 9% NaCl, 1.5 hours at 850°C., 0.24 cu.ft./minute, dry air flow.

2. 200 ml. of H_2O per 100 grams roasted ore at 80°C.

Uranium Contents of the Water Leach Solution - The extraction of uranium into the water leach for the most part is negligible, i.e., only a few tenths of one percent. However, when roasting under a variety of conditions, uranium has, from time to time, appeared in the water leach.

For a number of selected tests, a tabulation of the uranium contents of water leach solutions as a function of roasting conditions is presented in Table 19. Close observation of the tabulated results shows that the uranium extractions are, in general, affected by at least two roasting variables, i.e., the contact of air with the charge (bed-depth) and the time of the roast. It is also indicated that uranium is not solubilized by low temperature roasts (600°C. or below) and that moisture aids in reducing the amount of water-soluble material.

Apparently uranium loss through the water leach would not be realized in normal plant operation with sufficient roasting time and air contact. Nevertheless, the possible escape of uranium through this channel suggests some plant control of these solutions. The uranium level is such that a micro analyses would be required, e.g., the fluorimetric method.

The reason for the occasional dissolution of uranium by the water leach has not been completely investigated. Limited tests indicate that there may be a correlation between carbonate content and uranium content of the solution (carbonate being supplied, perhaps, by formation of soluble Na_2CO_3 under certain roasting conditions).

Table 19

U in H_2O Leach

Run No.	Time (hrs.)	NaCl (%)	Temp. (°C.)	Bed Depth (in.)	Type Ore	Atmospheric Conditions	U (mg)	U** (% of Total)
H-255	0.0	8	850	1/4	Uravan	-	15.5	12.0
H-256	0.5	8	850	1/4	Uravan	-	5.5	4.2
H-169	1.5	8	875	1/4	Uravan	-	0.05	0.04
H-170	1.5	8	875	1-1/4	Uravan	-	2.7	2.1
H-168	2.5	8	850	2	Uravan	-	6.0	4.6
H-251	2.5	8	200	1-1/4	Uravan	-	0.4	0.3
H-252	2.5	8	600	1-1/4	Uravan	-	0.05	0.04
H-253	2.5	8	750	1-1/4	Uravan	-	18	14.0
H-254	2.5	8	900	1-1/4	Uravan	-	13	10.0
H-227	1.5	8	850	1/4	Uravan	air + 47 g. CO_2	0.1	0.08
H-228	1.5	8	850	1/4	Uravan	air + 470 g. CO_2	5.0	3.9
H-171	1.0	8	850	1-1/4	Indian Reservation	-	2.5	0.18
H-173	4.0	8	850	1-1/4	Indian Reservation	-	0.2	0.014
H-175	1.0	8	850	1-1/4	Indian Reservation	-	1.4	0.14
H-176	2.5	8	850	1-1/4	Indian Reservation	-	0.2	0.014
H-174	2.5	10	850	1-1/4	Indian Reservation	-	0.2	0.014
H-177	4.0	8	850	1-1/4	Indian Reservation	-	0.1	0.007
H-178	1.0	12	850	1-1/4	Indian Reservation	-	1.8	0.13
H-185	2.5	8	850	1-1/4	Wild Steer	-	8.0	2.9
H-186	2.5	10	850	1-1/4	Wild Steer	-	9.0	3.2
H-191	1.5	10	750	1/4	Wild Steer	-	0.04	0.014
H-192	1.5	10	850	1/4	Wild Steer	-	0.04	0.014
H-188	1.5	10	900	1/4	Wild Steer	-	0.15	0.05
H-193	1.0	8	850	1-1/4	Wild Steer	-	12.0	4.3
H-194	2.5	8	850	1-1/4	Wild Steer	-	1.5	0.5
H-195	4.0	8	850	1-1/4	Wild Steer	-	0.3	0.11

Table 19 (continued)

Run No.	Time (hrs.)	NaCl (%)	Temp. (°C.)	Bed Depth (in.)	Type Ore	Atmospheric Conditions	U (mg.)	U** (% of Total)
H-265*	1.5	8	825	1/4	Uravan	dry N_2	7.0	5.4
H-261*	1.5	8	825	1/4	Wild Steer	dry N_2	25.0	9.0
H-262*	1.5	8	825	1/4	Indian Reservation	dry N_2	40.0	2.9
H-263*	1.5	8	825	1/4	Cactus Rat, Lot 134	dry N_2	23.0	16.5
H-264*	1.5	8	825	1/4	Uravan	dry N_2	6.5	5.0
H-266*	1.5	8	825	1/4	Uravan	air + 2-5 g. H_2O	5.0	3.8
H-268*	1.5	8	825	1/4	Uravan	air + 15 g. H_2O	0.2	0.15
H-267*	1.5	8	825	1/4	Uravan	air + 27 g. H_2O	0.25	0.19
H-269*	1.5	8	825	1/4	Uravan	air + 58 g. H_2O	0.2	0.15

Roast Conditions:

1. 100 g. samples of ore ground to minus 20 mesh roasted with a total gas flow (dry air, dry air + CO_2, air and moisture or dry N_2 as indicated) of .24 CFM in a muffle furnace.

2. 1/4" beds were "heat-up" type roasts. 1-1/4" or 2" beds were "constant temperature type roasts.

Leach Conditions: 200 ml. of water per 100 g. ore for 2 hours at 80°C.

* H-265 - H-269 were roasted in a quartz tube heated by an external furnace.

** Percentages calculated from U in heads.

Other Considerations - Within wide limits of variation, such factors as pulp density and particle size have little effect on the vanadium extraction by water leaching. For plant operation, a simple percolation leach is normally used.

Acid Leaching of Water Leached Calcines

Rate of Dissolution of Uranium and Vanadium in the Acid Leach - Rates of dissolution of uranium and vanadium by acid leaching salt-roasted ores at 80°C. are depicted by the experimental results in Table 20. The experimental procedures employed for these tests were similar to those used for the H_2O leach experiments described above.

Table 20

Dissolution Rates of Uranium and Vanadium in Acid Leach of Calcines

Experiment No.	Conc. HCl (%)	Time (min.)	Tails U(%)	Tails V(%)
L-370A	5	5	0.03	0.20
L-370B	5	10	0.03	0.20
L-370C	5	20	0.03	0.19
L-370D	5	30	0.03	0.19
L-370E	5	90	0.03	0.19
L-370F	5	240	0.03	0.19

Essentially all of the "available" uranium is extracted almost immediately by dilute acid treatment. Vanadium extraction is also rapidly achieved. Other tests have shown that the extractions are about the same when the leaches were conducted at room temperature.

Impurities Dissolved by Acid Leach Solutions - Since such information is important to processes for recovering the mineral values from solutions, determinations have been made of the impurities dissolved in the acid leach solutions from several different ore calcines. These data are presented in Table 21. Analyses of representative head samples of the ores treated have been shown previously in Table 1.

Upon comparing the two tables, it may be observed that the calcium in the acid leach increases with increasing CaO in the head ore. Also, with high lime ores, the extractions of aluminum and silica are increased considerably.

Similar data for direct acid leachings of raw ores are reported in Table 8, PART II. By comparing these tables with Table 21, it may be noted that considerably less iron, calcium, and magnesium are extracted from the roasted ores than from the raw materials.

Influence of Acid Concentration - This topic is discussed in detail in a following section entitled "The Consumption of Hydrochloric Acid During Leaching".

Other Considerations - Recoveries by acid leaching are not affected within wide limits of variation by such factors as pulp density or particle size. A simple percolation leach is normally used

Table 21

Impurities Dissolved by the Acid Solutions

Exp. No.	Type of Ore	Extractions* by Acid Leach									
		Al		SiO_2		Fe		Mg		Ca	
		mg.	%	mg.	%	mg.	%	mg.	%	mg.	%
H-218	Uravan	19	1	0	<1	29	5	55	11	190	24
H-219	Cactus Rat-Lot 254	7	1	38	<1	12	1	100	19	155	21
H-220	Cactus Rat-Lot 134	11	1	47	<1	22	2	85	22	245	22
H-221	Cactus Rat-Lot 411	15	1	35	<1	55	5	100	42	410	26
H-316	Rifle	90	6	165	<1	26	2	55	4	105	9
H-317	Rifle	115	8	47	<1	35	3	70	5	120	11
H-314	Rico	210	14	285	<1	16	1	10	1	815	38
H-315	Rico	215	14	125	<1	16	1	5	1	740	34
H-310	Mineral Mountain-683	415	20	560	<1	28	3	75	8	530	19
H-311	Mineral Mountain-683	390	19	330	<1	29	3	80	9	480	17
H-312	Mineral Mountain-750	1010	28	1750	2	80	12	160	18	2100	52
H-313	Mineral Mountain-750	830	23	1885	2	90	13	200	22	2005	50

Roast Conditions: 100 gms. ore ground to minus 20 mesh roasted with 8% NaCl for 1.5 hours at 850°C. and a .24 cfm dry air flow over a 1/4" bed (heat-up).

H_2O Leach Conditions: 200 ml. H_2O per 100 g. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. 5% HCl per 100 g. ore for 2 hours at 80°C.

* Percentages calculated from head analysis (see Table 1).

in plant practice.

Processing of Several Ores with an Optimum Combination of Conditions

Using the most optimum conditions, as suggested by the data presented above, a number of different ores were treated by the salt-roast, acid-leach method. Experimental results are presented in Table 22.

The recoveries were exceptionally good for all of the high vanadium, low lime ores. Over-all recoveries were also good from the high lime ores, but the vanadium extractions by the water leach were affected in the manner described previously.

Only one ore (Cactus Rat-Lot 254) failed to respond to the acid process in the expected manner (i.e., the uranium recoveries were low). This ore is different from the other ores treated in that the vanadium content was quite small (only 0.5% V_2O_5). By tests not shown in Table 22, it has been demonstrated that the recoveries can be increased to an acceptable level by lowering the roast temperatures from 850°C. to 800°C., or decreasing the NaCl concentration from 8 to 6%.

Apparently the vanadium concentration, at low levels, has a certain influence on the acid process. This phenomenon was not given further consideration since it would not, in any case, be economically feasible to treat ores of such low vanadium content by the salt-roast, acid-leach process.

Table 22

Leaching of Roasted Ores

Exp. No.	Source of Ore	Extractions: H_2O Leach V % of Total	Extractions: Acid Leach U % of Total	Extractions: Acid Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
H-152	Uravan	80	94	9	0.007	6	0.110	11
H-181	Indian Reservation	74	99	20	0.016	1	0.093	6
H-192	Wild Steer	85	97	9	0.009	3	0.127	6
H-198	Cactus Rat-Lot 134	72	94	13	0.009	6	0.120	15
H-199	Cactus Rat-Lot 134	71	96	14	0.006	4	0.126	15
H-200	Cactus Rat-Lot 411	56	91	28	0.006	9	0.126	16
H-201	Cactus Rat-Lot 411	58	90	26	0.008	10	0.123	16
H-196	Cactus Rat-Lot 254	44	72	21	0.030	27	0.108	35
H-270	Cactus Rat-Lot 254	42	64	17	0.043	35	0.104	40
H-355	Rico	47	88	45	0.006	12	0.102	8
H-357	Rico	51	91	41	0.006	9	0.109	8
H-354	Rifle	86	98	6	0.001	2	0.091	8
H-356	Rifle	-	98	-	0.002	2	0.105	-
H-310	Mineral Mountain-683	53	88	32	0.017	12	0.127	15
H-311	Mineral Mountain-683	52	89	34	0.016	11	0.125	14

Procedure:

1. 100 g. ore, containing 8% NaCl, ground to minus 20 mesh.
2. Samples were given a heat-up period (400-850°C.) and held for 1.5 hours at 850°C. and a .24 cfm dry air stream was maintained during roast. Sample bed depth was 1/4".

Water Leach Conditions: 200 ml. of H_2O per 100 g. ore for 2 hours at 80°C.

Acid Leach Conditions: 200 ml. of 5% HCl per 100 g. ore for 2 hours at 80°C.

The Production of Hydrochloric Acid During Roasting

Introduction

In the processing of carnotite and roscoelite ores for uranium and vanadium by the salt-roast process, appreciable quantities of hydrochloric acid are formed during the roast by reactions between certain mineral constituents, sodium chloride, and water. In plants which utilize the water leach for vanadium and a subsequent acid leach for uranium, water scrubbing of the roast gases provides a cheap and convenient source of acid leach solution. For processing normal ores (1-2% CaO), it has been found in plant operations that the amount of hydrochloric acid recovered from the roast gases is approximately sufficient to furnish the acid required in the leaching of the calcine. For ores with slightly higher lime content, some sulfuric acid must be used to fortify the hydrochloric acid solution.

In anticipation of processing ores of considerably higher content (4-6% CaO), it was apparent that the increased acid requirement would constitute an appreciable increase in processing costs. This fact prompted a study of the acid problem involved in the salt-roast, acid-leach process, namely, a study of the factors affecting the production of hydrochloric acid during roasting, and the consumption of hydrochloric acid during leaching. The latter of these topics will be discussed in a separate section.

In studying, on a laboratory scale, the effect of the more common variables on hydrochloric acid production, a set of standard

roasting conditions were chosen to correspond as nearly as possible with conditions used in plant operations. As a means of comparing the data obtained in the laboratory apparatus with actual plant operational figures, the personnel at the Rifle Plant conducted careful tests over a period of several days to determine the total amount of HCl evolved in the roast gases per unit weight of ore. These tests indicated that under optimum conditions of roasting and with total absorption of the hydrochloric acid, an average yield of 50 pounds of HCl per ton of ore could be obtained from the multiple-hearth roaster. The Rifle ore, when tested in the laboratory apparatus, was found to yield 54 pounds of HCl per ton of ore. The excellent agreement between these two values indicates that the standard conditions chosen for the laboratory tests should provide data representative of plant operations.

Experimental Methods

The roast was carried out in a two-inch quartz tube which was surrounded by a cylindrical muffle furnace. The charge, usually consisting of 100 gm. of -20 mesh ore and 9 gm. of finely ground sodium chloride, was contained in a platinum boat. The temperature was measured by an alumel-chromel thermocouple placed in a quartz tube and embedded in the charge. Appropriate connections permitted entrance and exit of gases. The rate of air flow was measured by a rotameter. The air was freed of water and carbon dioxide by passing through successive columns of concentrated H_2SO_4, ascarite, and drierite, and was preheated before entering the reactor tube. Known amounts of water vapor were added when desired

by passing the dry air stream through water held at a constant temperature and contained in a vessel which could be accurately and easily weighed.

The exit gases were passed through a glass wool plug at the end of the reactor tube, thus removing all dust and most of the sublimed salts, and into approximately 1 liter of 0.2 N NaOH solution contained in three 500 ml. gas scrubbing bottles. This solution was found to remove effectively any HCl, Cl_2, or CO_2 in the roast gases.

The entire system was maintained under slight vacuum by applying suction at the final gas scrubbing bottle. This practice minimized any small leaks that might be present in a system containing so many glass joints and rubber connections.

The three alkaline scrubber solutions were combined in a measured volume and aliquots of this solution were used to determine the total chlorine absorbed either as HCl or free chloride, and the chlorine absorbed as free chlorine. In isolated experiments, the solution was also analyzed for carbonate or sulfate.

The free chlorine was determined by an iodometric method - an excess of potassium iodide was added to an aliquot, the solution acidified with dilute H_2SO_4 and the liberated iodine titrated directly with sodium thiosulfate solution.

The total chlorine was determined by first reducing quantitatively the hypochlorite ion (ClO^-) to the chloride ion by adding a slight excess of sodium arsenite ($NaAsO_2$) to the original basic solution, then precipitating the chloride as the silver salt in a nitric acid solution

and weighing as AgCl.

A more simple but less accurate method for determining the hydrochloric acid absorbed may be employed provided the free chlorine content is practically nil. This consists of using a known amount of sodium hydroxide in the scrubbers and determining the excess after the absorption of the HCl by simple titration. The presence of free chlorine interferes with the end point in this titration. Also, the absorption of CO_2 in the scrubbers affects the titration somewhat, but may be compensated for by titrating to a pH of 4.0.

The standard conditions which were chosen for the roasting treatment may be summarized as follows:

Ore Sample	100 gm. Uravan Stockpile
NaCl Concentration	9 gm. NaCl/100 gm. of ore
Roasting Temperature	Heat-up Time* Plus 90 min. at Temperature
Air Flow	0.2 cu. ft./minute.
Moisture in Air Stream	1.0 gm. H_2O/cu. ft. of air.
Bed-Depth	0.6 cm.
Pressure	1-1/2" Hg less than Atmospheric.
Particle Size of Ore	-20 Mesh

*Heat-up time was approximately 20 minutes.

In determining the influence of each of these variables on HCl production, all other variables were held constant while the one

being studied was varied over a wide range.

Influence of the Roast Atmosphere

The roast atmosphere during plant operations contains appreciable quantities of moisture, large quantities of carbon dioxide, and very small quantities of sulfur dioxide, along with a large excess of air. The moisture, carbon dioxide, and sulfur dioxide originate primarily as combustion products of the coal used as fuel for the roasting operations. The influence of each of these impurities on the production of HCl was determined.

From a knowledge of the amount of coal burned and the stack gas flow per unit weight of ore processed, and assuming an average value for the hydrogen content of the coal and the humidity of the region, it may be calculated that from 8 to 12 gm. of water per 100 gm. of ore, or 0.7 to 1.0 gm. of water per cu. ft. of stack gas, passes through the multiple-hearth roaster.

In the laboratory, tests were conducted in which the moisture in the air stream varied from 0.0 to 68 gm. of water per 100 gm. of ore. The results are depicted graphically in Figure 1. It may be observed that small concentrations of moisture increase the yield markedly above that obtained with dry air. However, at concentrations near those estimated for plant conditions, the yield levels off at a fairly constant value. These data indicate that water plays an important role in the formation of HCl during the roast. In the ascending portion of the curve, an excess of water is not contacting the ore, while in the flat portion, an excess of water is contacting the ore.

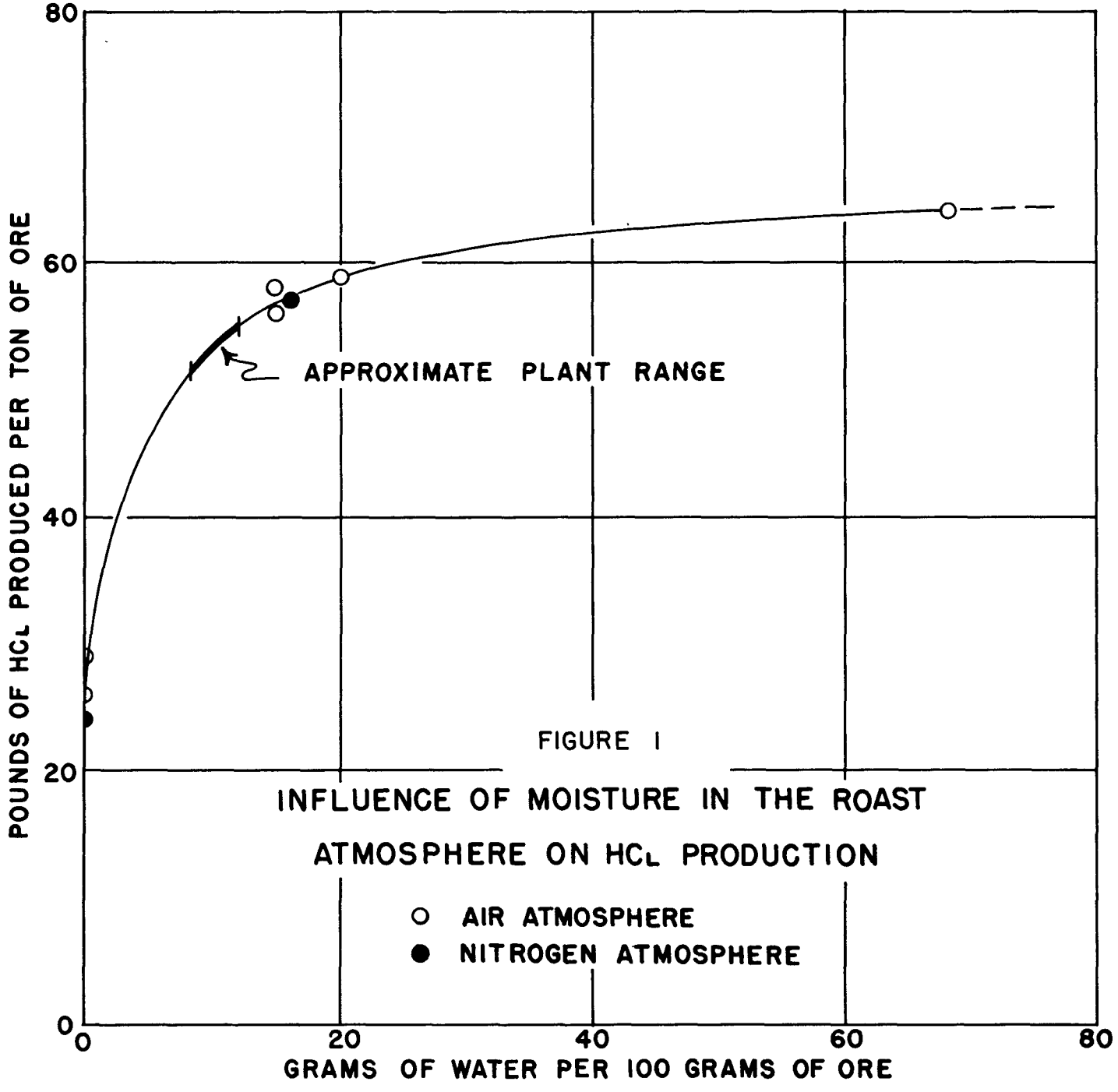


FIGURE I

INFLUENCE OF MOISTURE IN THE ROAST ATMOSPHERE ON HCL PRODUCTION

Also, reported in Figure 1, are two points which were obtained by using a nitrogen atmosphere entirely free of oxygen. It is of significant interest to note that with equal concentrations of moisture, the yield of HCl is approximately the same with the nitrogen atmosphere as with the nitrogen-oxygen (air) atmosphere. This indicates that oxygen plays a minor role in the reactions by which HCl is formed during the roast. It also serves to emphasize that moisture plays a major role in the formation of HCl.

Another important bit of information may be gained from the roasts in a nitrogen atmosphere. Although the total amount of chlorine evolved in a nitrogen atmosphere is the same as that for a nitrogen-oxygen atmosphere, no free chlorine was present in the nitrogen runs, whereas, considerable quantities were present in the nitrogen-oxygen runs. This is evidence that HCl rather than free chlorine is the product of the original reactions which take place during the roast. The presence of free chlorine in the roast gases during a normal roast is probably the result of a secondary gas phase reaction between HCl and O_2 to form free chlorine and water ($4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$).

It may be calculated that about 40 gm. of CO_2 per 100 gm. of ore passes through the roaster during plant operation. Laboratory tests in which CO_2 was passed over the ore bed in this amount indicated that this compound exerts no effect upon HCl formation during roasting.

It may be estimated that about 0.2 gm. of sulfur dioxide per 100 gm. of ore passes through the roaster during plant operation.

Experiments in which SO_2 was bled into the air stream in quantities 5 to 10 times this amount, indicated that this compound serves to increase the yield of HCl significantly. This suggests that burning of highly pyritic coal or roasting with pyrite would provide a means of increasing the HCl production. However, consideration of the economics of such a process appeared unfavorable when compared with the cost of the sulfuric acid which it would save.

Influence of Sodium Chloride Concentration

In plant operations, the roaster feed contains from 7 to 9% NaCl. This is from 5 to 10 times the theoretical amount required to convert the vanadium to a water-soluble form. Upon varying the salt concentration from 3% to 15% in the laboratory apparatus, it was found that the yield of HCl increased quite regularly with NaCl concentration up to about 9% NaCl, then leveled off at a constant value, as illustrated in Figure 2. Apparently, above the 9% level, the sodium chloride concentration is in such excess that the yield of HCl is no longer affected by additional NaCl, but is dependent only upon the concentration of certain mineral constituents of the ore.

The minimum amount of salt required to yield the maximum quantity of HCl probably varies somewhat with the different ores, being primarily dependent on the lime content of the ore. For example, it was found that the yield of HCl from an ore containing 5.0% CaO can be increased significantly by increasing the salt concentration from 9% to 12%.

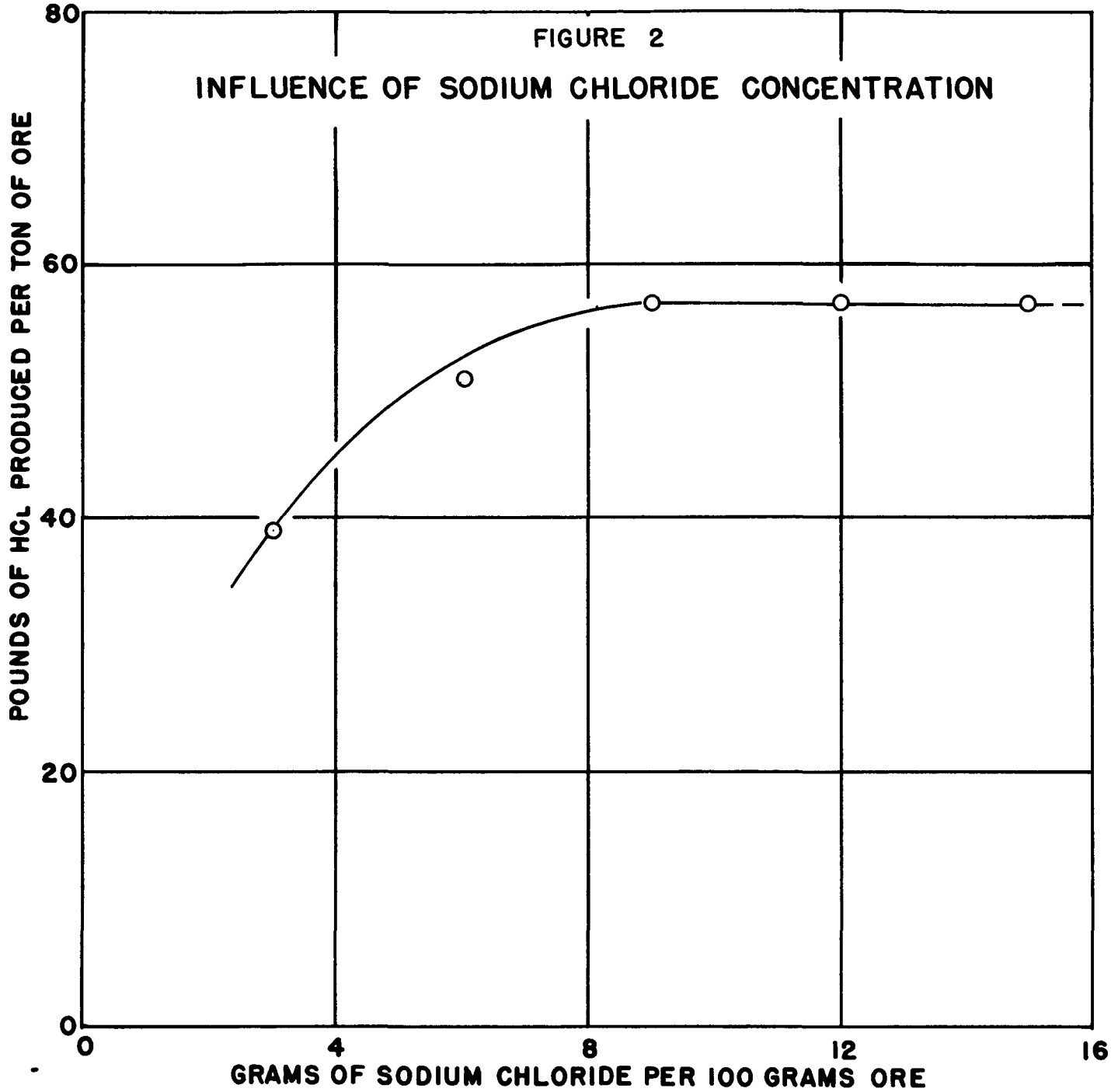


FIGURE 2
INFLUENCE OF SODIUM CHLORIDE CONCENTRATION
POUNDS OF HCL PRODUCED PER TON OF ORE
80
60
40
20
0
0
4
8
12
16
GRAMS OF SODIUM CHLORIDE PER 100 GRAMS ORE

Influence of Roasting Temperature

In the multiple-hearth roaster used in plant operations, the total residence time of the ore in the roaster is about 2 hours. There is a gradation of temperature between the various hearths, but it has been estimated that the ore is held at about 750°C. for the first 30 to 45 minutes, then at 850°C. for the remaining 75 to 90 minutes. For the laboratory tests, a temperature of 850°C. was chosen as standard with a roasting time of 90 minutes (plus a heat-up time of approximately 20 minutes).

Upon conducting roasts at temperatures from 750°C. to 900°C., it was found that the yield of HCl during the 90 minute roasting period increased markedly with temperature. The data are shown graphically in Figure 3. It may be noted that the yield was doubled upon increasing the temperature from 750°C. to 850°C.

Influence of Ore Bed-Depth

In the multiple-hearth roaster, the ore is continuously rabbled, while in the laboratory experiments it was necessary to use a static bed. Consequently, it was difficult to compare the gas-solid contact variable in the two systems. However, data have been collected to illustrate the importance of intimate contact of the gases with the ore particles by varying the bed-depth of a given charge of ore during an otherwise standard roasting treatment. As shown graphically in Figure 4, the yield of HCl is approximately halved by increasing the bed-depth from 0.4 to 4.0 cm. Since the yield in the deeper beds appears to decrease toward that ob-

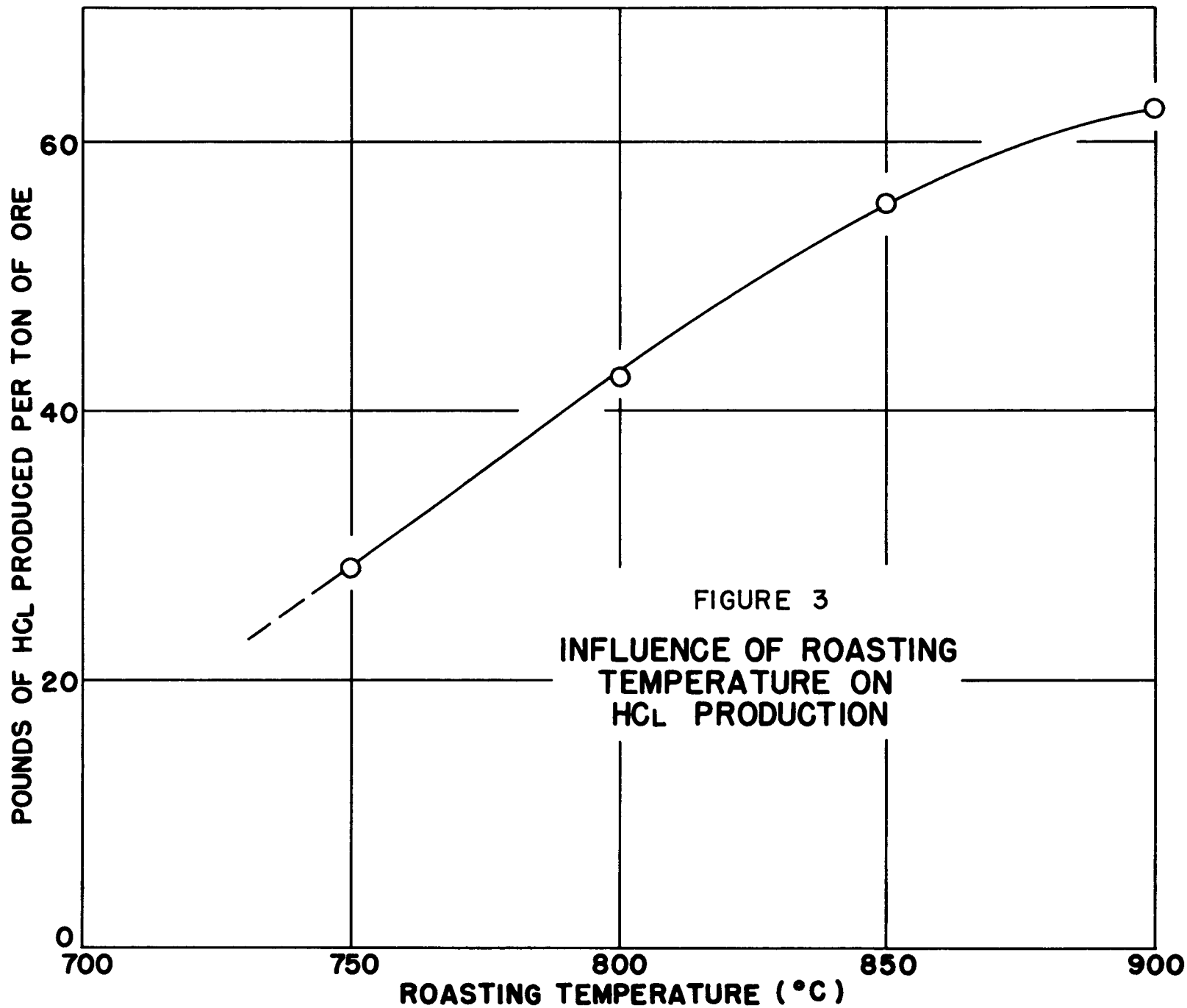


FIGURE 3

INFLUENCE OF ROASTING TEMPERATURE ON HCL PRODUCTION

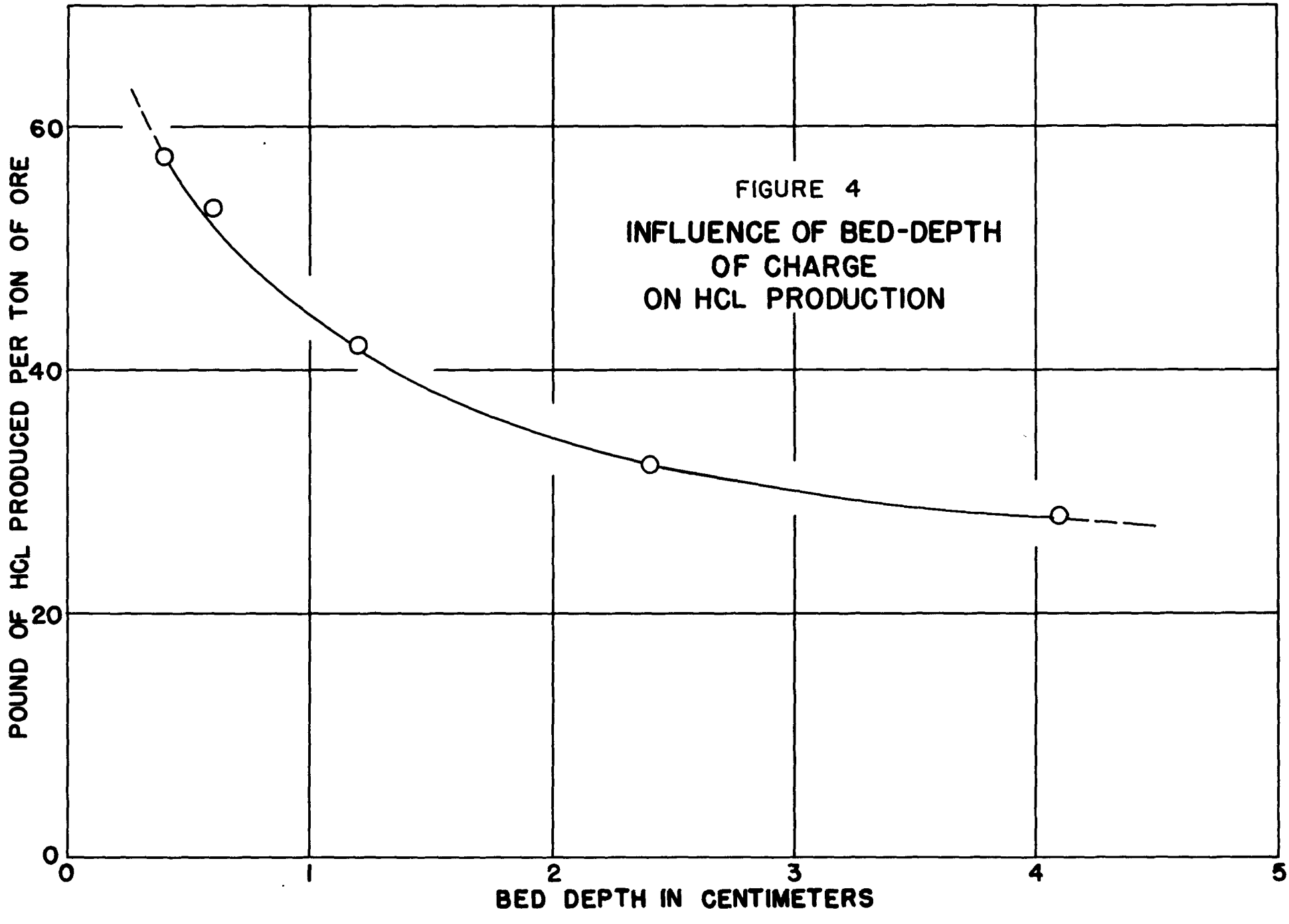


FIGURE 4

INFLUENCE OF BED-DEPTH OF CHARGE ON HCL PRODUCTION

tained with dry air, it may be surmised that increasing the bed-depth merely decreases the contact of water vapor with the ore particles, thus decreasing the HCl production during any given time of roast.

The fact that the yield of HCl from Rifle ore was found to be about the same in the multiple-hearth roaster as in the laboratory apparatus, as was explained previously, may be interpreted to mean that the gas-solid contact in the deeper, but continuously rabbled, beds of the multiple-hearth roaster is about the same as in the thin, static beds used in the laboratory tests.

Influence of Ore Mesh Size

The samples used in determining the effect of the particle size of the feed material on HCl production were prepared by total grinding of uniform samples of ore to pass screens of various mesh size. In this way, the concentration of mineral constituents was held constant and did not enter as a second variable. As may be observed in Table 23, the -60, -80, and -100 mesh material produced about the same amount of HCl per unit weight of ore, while -20 mesh material gave a slightly lower yield. Apparently, the maximum yield of HCl can be obtained if the ore is ground to the natural grain size of the silica particles.

Table 23

Effect of Particle Size of Ore on HCl Production

Exp. No.	Crushed to:	lbs. HCl/ton of ore
L-409	-20 mesh	54
L-424	-60 mesh	60
L-422	-80 mesh	64
L-420	-100 mesh	61

Another series of runs was made in which -20 mesh material was screened into various fractions and a sample of each fraction subjected to the standard procedure. These data are given in Table 24. In general, it was found that the HCl production ran parallel to the concentration of vanadium and uranium in the various fractions. The smaller particle size fractions were found to contain concentrations of vanadium and uranium and produced greater quantities of HCl.

Table 24

Contribution of Various Size Fractions to HCl Production

Exp. No.	Size Fraction	Sieve Analysis	lbs. HCl/ton
L-414	20-40 mesh	15	44
L-418	40-60 mesh	26	53
L-410	60-100 mesh	34	56
L-416	-100 mesh	25	80

Rate of Reaction Studies

The study of the roasting time variable provided very interesting information on the rate at which the HCl is formed during the roast. In securing these data, the amounts of HCl evolved during each of several short time periods of a continuous roasting treatment were determined.

It may be observed in Figure 5, that a yield of 40 pounds of HCl per ton of ore is obtained during the heat-up period plus 30 minutes at 850°C. Another 60 minutes roasting, making a total of 90 minutes at temperature, increased this yield to 57 pounds per ton, while still another 30 minutes further increased the yield to 63 pounds per ton.

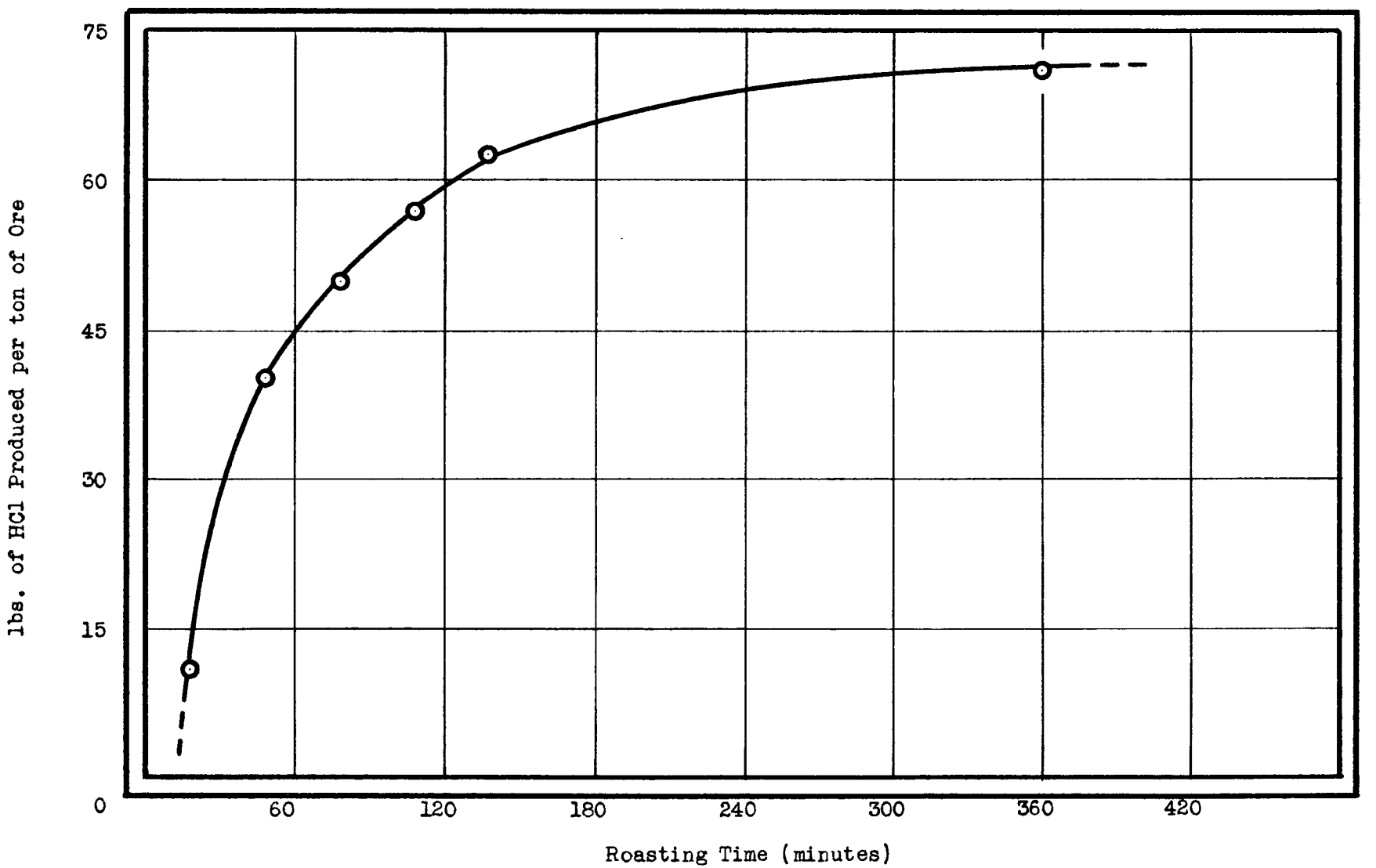


Figure 5 . Effect of Roasting Time on HCl Production

Continued roasting for a total time of 6 hours gave a total yield of 71 pounds of HCl per ton of ore.

It is evident, therefore, that the bulk of the HCl is evolved during the first 90 minutes of the roast, and that a nominal increase in roasting time will not improve the yield greatly.

Perhaps, a more useful manner of presenting these data is illustrated in Figure 6 in which the logarithm of the HCl production value is plotted against time for a normal roasting treatment. It is apparent that such a plot results in a straight line over the major portion of the reaction. Upon extrapolating this line to the approximate time at which evolution of HCl began, the over-all yield of HCl can be resolved into two quantities, (1) that formed by fast reactions during the early stages of the roast, and (2) that formed by slow reactions which proceed at a steady rate over the entire roasting period.

In the case of Uravan ore, the initial fast reactions account for about 30 pounds of HCl/ton, or nearly 50% of the yield obtained during the normal 90 minute roast.

In the study of variables relating to the composition of the ore, the rate of reaction approach proved quite useful as will be observed in later discussions.

Influence of Various Constituents of the Ore

A number of experiments were conducted to determine with some degree of certainty the role played by various constituents of the ore in the formation of HCl during roasting. In general, the procedure con-

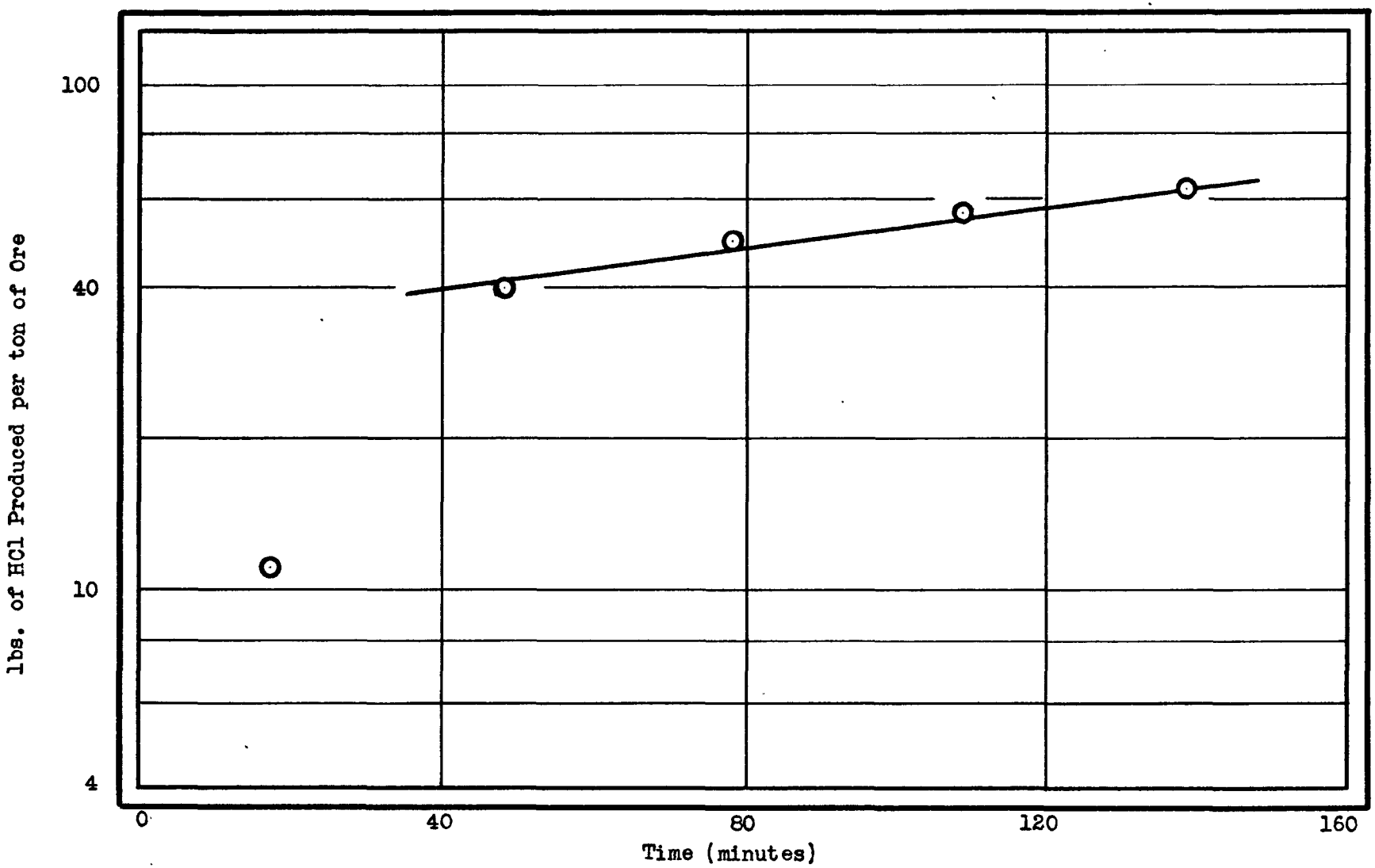


Figure 6 . Rate of Reaction Studies on Uravan Ore

sisted of adding to a normal charge various metallic constituents in the form of the oxide or the carbonate, and noting the effect on the amount of HCl evolved.

The influence of calcite (or lime) content of the ore on HCl production was studied early in the investigation by adding pure $CaCO_3$ to Uravan ore and carrying out the roast in the usual manner. When ores with varying and sufficiently high calcite content became available, this effect was measured in a more reliable manner by testing the actual ores. The data shown graphically in Figure 7 provide an excellent illustration of the dependence of HCl production on lime content of the ore. The HCl production from these ores appears to be a linear function of the lime content. An increase of 1% in the CaO content tends to decrease the HCl production by about 10 pounds per ton.

It should be mentioned that the V_2O_5, Fe_2O_3, and MgO contents do not differ widely from these ores, and this fact may contribute to the apparent linear dependence on lime content.

It may also be observed that the synthetic mixtures of Uravan ore with $CaCO_3$ yielded results in excellent agreement with those obtained with the actual ores.

As for the manner in which calcite inhibits the formation of HCl, some information may be gained by referring to Figure 8, and Table 25, which give the rate of reaction data on ores of varying lime content. It is obvious that the steady slow reactions proceed at about the same rate regardless of the lime content of the ore, but that the initial fast reactions are inhibited markedly, being nullified almost completely

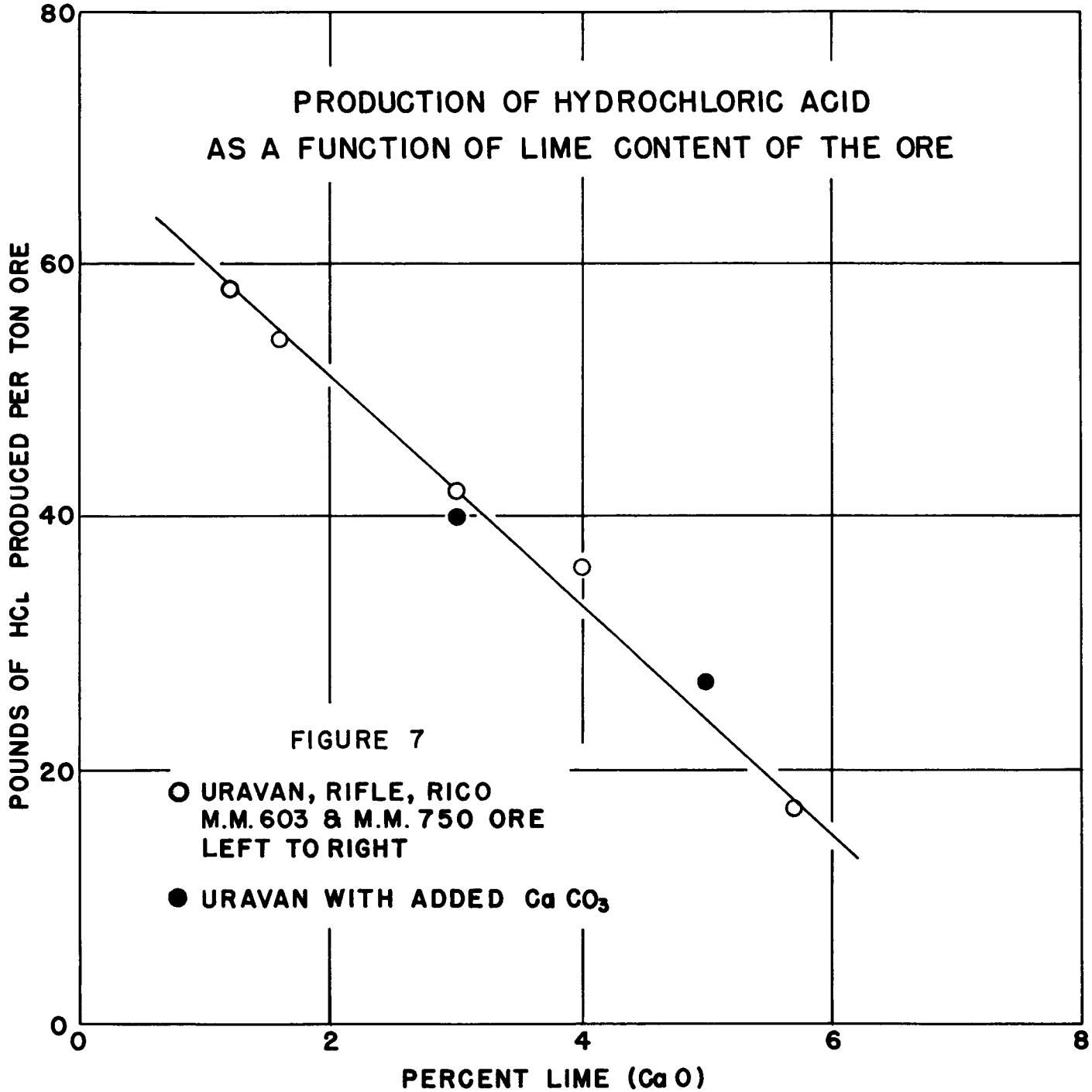

PRODUCTION OF HYDROCHLORIC ACID
AS A FUNCTION OF LIME CONTENT OF THE ORE
POUNDS OF HCL PRODUCED PER TON ORE
80
60
40
20
0
0
2
4
6
8
PERCENT LIME (CaO)
O URAVAN, RIFLE, RICO
M.M. 603 & M.M. 750 ORE
LEFT TO RIGHT
● URAVAN WITH ADDED Ca CO3

FIGURE 7

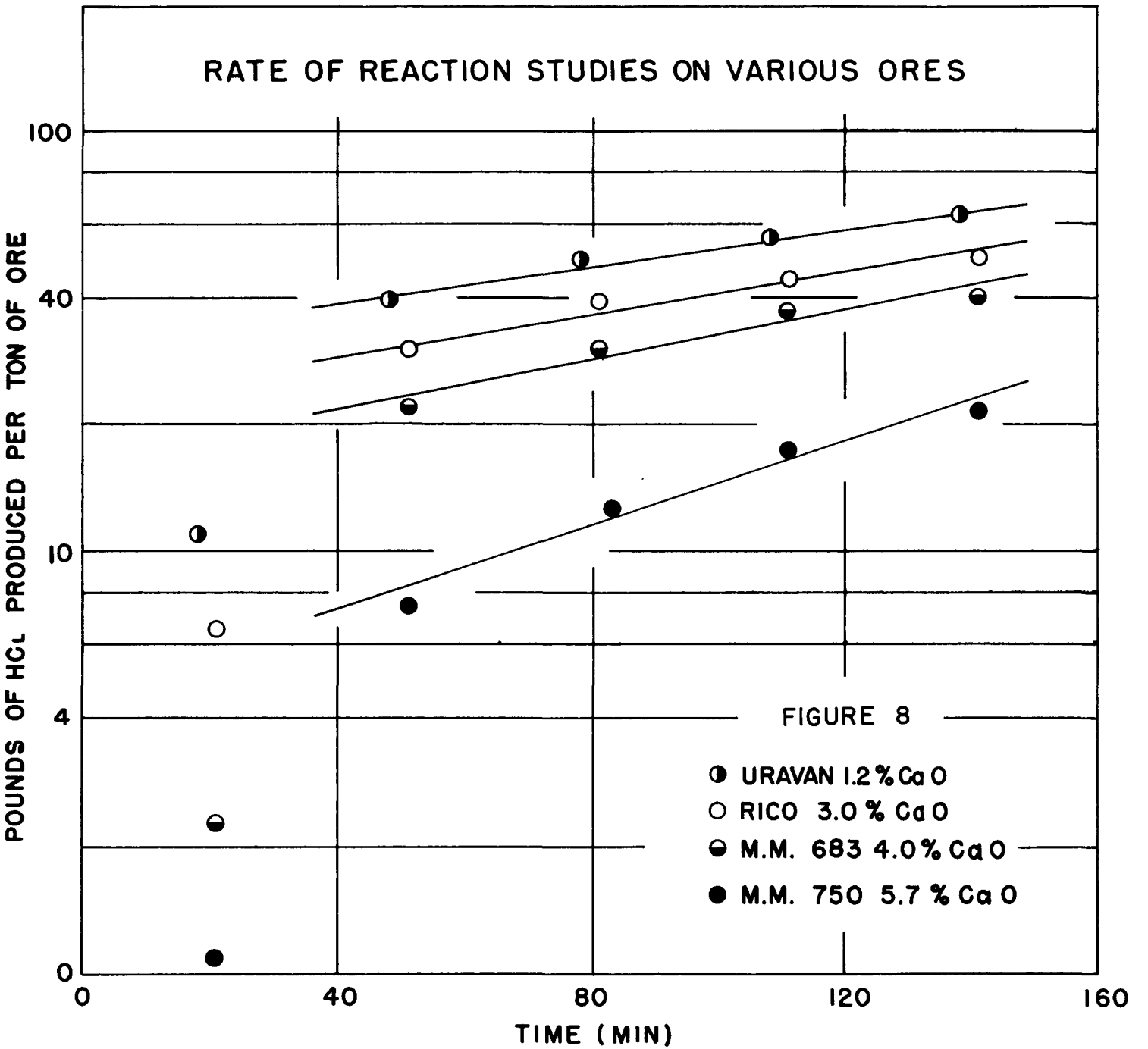

RATE OF REACTION STUDIES ON VARIOUS ORES
POUNDS OF HCL PRODUCED PER TON OF ORE
100
40
10
4
0
0
40
80
120
160
TIME (MIN)
URAVAN 1.2% CaO
RICO 3.0% CaO
M.M. 683 4.0% CaO
M.M. 750 5.7% CaO

FIGURE 8

with about 5.0% CaO.

The initial fast evolution of HCl during the normal roast is probably due to reactions between quite reactive vanadium minerals, sodium chloride, and water. For example, vanadium present as vanadyl-vanadate reacts readily with NaCl and water to form sodium vanadate and hydrochloric acid, as will be shown in a later section. In the presence of $CaCO_3$, it is probable that the vanadyl-vanadate is converted to calcium-vanadate, which reacts to form HCl very slowly, if at all.

Table 25

Production of HCl from Various Types of Ore

Exp. No.	Type of Ore	% CaO in Ore	Total lbs. HCl per ton of ore	lbs. HCl per ton Fast Reaction	lbs. HCl per ton Slow Reaction
L-410	Uravan	1.2	58	32	26
L-430	Uravan + $CaCO_3$	3.0	40	11	29
L-435	Uravan + $CaCO_3$	5.0	27	0	27
H-329	Rifle	1.6	57	32	25
H-346	Rico	3.0	43	20	23
H-345	Mineral Mountain-683	4.0	37	15	22
H-343	Mineral Mountain-750	5.7	17	4	13

As for the major metallic constituents of the ore, it was found that magnesium oxide and ferric oxide exerted a slight inhibiting action on the initial fast reactions by which HCl is formed, but over a roasting period of 90 minutes, no significant effect was observed. Alumina produced no significant effect on the initial fast reactions or the over-all 90 minute production figure. These data are recorded in Table 26.

Table 26

Effect of Various Metallic Oxides on HCl Production

Exp. No.	Description of Run	Total lbs. HCl/ ton	lbs.HCl/ ton Fast Reaction	lbs.HCl/ ton Slow Reaction
L-434	Normal Uravan*	57	29	28
L-519	Duplicate on Uravan	59	31	28
L-430	$CaCO_3$ added to give 3.0% CaO	40	11	29
L-512	MgO added to give 1.7% MgO	56	12	44
L-465	Fe_2O_3 added to give 1.8% Fe_2O_3	55	18	37
L-511	Al_2O_3 added to give 6.5% Al_2O_3	61	28	33

*Uravan head contained 1.2% CaO, 0.85% MgO, 0.9% Fe_2O_3, and 3.25% Al_2O_3.

Normal carnotite ores contain 83 to 87% silica. Upon subjecting samples of pure sea sand to the standard roasting treatment, it was found that 10 pounds of HCl per ton of sand were produced. There was no evidence of an initial fast reaction, and the steady reaction was much slower than that obtained for normal carnotite ores. Apparently, the silica, salt, water reaction, $SiO_2 + 2NaCl + H_2O \longrightarrow Na_2SiO_2 + 2HCl$, plays a minor, but significant, role in the production of HCl. This does not eliminate the possibility that certain complex silicates are contributing greatly to the HCl production. This will be discussed in a later section.

Nature of the Reactions by which HCl is Formed during Roasting

After determining the influence of roasting conditions and of certain basic constituents of the ore on HCl production, it became of interest to ascertain in so far as possible the nature of the reactions

by which the HCl is formed during the roast, i.e., the mineral or minerals which contribute to the formation of HCl.

It was mentioned that the silica, salt, water reaction contributes about 10 lbs. of HCl per ton or 0.014 moles HCl/100 gm. The average yield from Uravan ore is 57 pounds of HCl/ton or 0.078 moles HCl/100 gm. Upon consideration of the various minerals present in carnotite and roscoelite ores, it seemed quite probable that most of the remaining 45 to 50 pounds of HCl originates from reactions between vanadium minerals, salt, and water. Accordingly, a number of experiments were conducted in which various vanadium compounds were added to pure silica or to Uravan ore and the effect on HCl production noted. The data are compiled in Table 27.

Vanadium Pentoxide - The first vanadium compound thus studied was vanadium pentoxide. As illustrated by the following equations, the amount of HCl formed is dependent on whether meta-, pyro-, or ortho-vanadate is produced by the reaction:

$$(1)\ V_2O_5 + 2NaCl + H_2O \longrightarrow 2NaVO_3 + 2HCl$$

$$(2)\ V_2O_5 + 4NaCl + 2H_2O \longrightarrow Na_4V_2O_7 + 4HCl$$

$$(3)\ V_2O_5 + 6NaCl + 3H_2O \longrightarrow 2Na_3VO_4 + 6HCl$$

Experimentally, it was found that the addition of 0.020 mole of vanadium in the form of V_2O_5 to 100 gm. of Uravan ore resulted in an average increase in HCl production of 0.021 mole. Addition of this same quantity of V_2O_5 to 100 gm. of pure sand also increased the HCl production

Table 27

Influence of Various Compounds on HCl Production

Charge		Material Added		HCl Production (moles HCl)	Increase in HCl Production (moles HCl)	moles HCl Increase per mole V
100 gm. of:	moles V in Charge	Type of Compound	moles V			
Uravan	0.02	none	none	0.078[1]		
Sea Sand	none	none	none	0.014		
Uravan	0.02	V_2O_5	0.02	0.099[2]	0.021	1.05
Sea Sand	none	V_2O_5	0.02	0.035	0.021	1.05
Uravan	0.02	$NaVO_3$	0.02	0.079	0.001	0.0
Uravan	0.02	$Fe(VO_3)_3$	0.02	0.096[3]	0.018	0.90
Sea Sand	none	$Fe(VO_4)$	0.02	0.036	0.022	1.10
Uravan	0.02	Red Cake	0.02	0.095[4]	0.017	0.85
Sea Sand	none	Red Cake	0.02	0.033	0.019	0.95
Sea Sand	0.02	Carnotite Mineral	0.02	0.054	0.040	2.00
25 gm. of Montmorillonite	none	none	none	0.027 (78 lbs. HCl/ton)		

(1) Average of four determinations.

(2) Average of two determinations.

(3) Average of three determinations.

(4) Average of two determinations.

by 0.021 mole. These data constitute excellent evidence that vanadium pentoxide reacts with sodium chloride and water during the roast to form sodium meta-vanadate and hydrochloric acid as represented by equation (1).

Sodium Meta-Vanadate - In another experiment in which 0.02 mole of vanadium in the form of sodium meta-vanadate was added to the charge, it was found that the HCl production was not affected. This supports the previously discussed data on V_2O_5, in that it shows the meta-vanadate to be stable under the roasting conditions. If the meta-vanadate had been converted to the pyro- or ortho-vanadate, an increase in HCl production would have resulted, as illustrated by equations (4) and (5):

$$(4)\ 2NaVO_3 + 2NaCl + H_2O \longrightarrow Na_4V_2O_7 + 2HCl$$

$$(5)\ 2NaVO_3 + 4NaCl + 2H_2O \longrightarrow 2Na_3VO_4 + 4HCl$$

Iron Vanadate - As may be noted in the folow sheet for the salt-roast, acid-leach process, the vanadium which dissolves along with the uranium in the acid leach liquor is eventually precipitated as an iron vanadate and recycled through the roaster. It was of interest to determine the effect of this recycle material on HCl production.

The iron vanadate was precipitated from two different vanadate solutions, one a meta-vanadate, the other an ortho-vanadate. The precipitate obtained by mixing solutions of sodium meta-vanadate and ferric nitrate was found to increase the HCl production on an average of 0.018 mole HCl per 0.020 mole of vanadium added. The most probable reaction is as follows:

$$(6)\ 2Fe(VO_3)_3 + 6NaCl + 3H_2O \longrightarrow Fe_2O_3 + 6NaVO_3 + 6HCl$$

The precipitate obtained in a similar manner from a sodium ortho-vanadate solution was found to increase the HCl production by 0.022 mole HCl per 0.020 mole of vanadium. The most probable reaction is as follows:

$$(7)\ 2FeVO_4 + 2NaCl + H_2O \longrightarrow Fe_2O_3 + 2NaVO_3 + 2HCl$$

In each of the above reactions involving iron vanadate, it may be noted that the HCl production is increased by 1 mole of HCl per 1 mole of vanadium. If the pyro-vanadate, $Na_4V_2O_7$, or the ortho-vanadate, Na_3VO_4, had been formed, the increase should have been 2 moles HCl and 3 moles HCl, respectively, per mole of vanadium.

As has been previously pointed out, all additional vanadium recycled through the roaster as iron vanadate is dissolved by the water leach. This is good evidence that the iron vanadate is completely converted to a sodium vanadate, though it gives no information as to the type of vanadate.

In summarizing, it may be said that the practice of recycling the the iron vanadate from the acid leach liquor tends to increase the yield of HCl by 1 mole HCl per mole of vanadium added. This would provide a means of increasing significantly the HCl production except for the fact that the quantity of vanadium coming out in the acid leach is quite small. It may be calculated that the normal recycle as currently practiced causes an increase of 2 to 3 pounds of HCl per ton of ore.

"Red-Cake" - The vanadium compound, commonly called sodium polyvanadate, which is precipitated from the water leach solution has the approximate formula: $2Na_2O \cdot 7V_2O_5$. The effect of this substance on HCl production was determined. It was found that 0.020 mole of vanadium as red-cake increased the HCl production by 0.017 mole HCl. The experimental data indicate definitely that the most probable reaction involves the formation of the meta-vanadate as shown by the following equation:

$$(8)\ 2Na_2O \cdot 7V_2O_5 + 10NaCl + 5H_2O \longrightarrow 14NaVO_3 + 10HCl$$

On the surface, it might appear that recycle of this readily available material would be a means of increasing the HCl production, but further consideration reveals that the increase in HCl production is less than the equivalent amount of H_2SO_4 required in precipitating red-cake from the water leach solution (see flowsheet for Rifle process).

Carnotite Mineral - In order to study the reaction of the carnotite mineral with sodium chloride and water, a high grade product was obtained by careful hand-picking from Indian Reservation ore. The empirical formula for the carnotite mineral has been determined by various investigators to be $K_2O \cdot 2UO_3 \cdot V_2O_5$. Chemical analysis of the hand-picked material gave a vanadium to uranium molar ratio of 1.1, which is in agreement with the formula and, therefore, indicated that practically no vanadium was present other than that in the carnotite mineral. The analysis indicated the material to be about 50% carnotite and 50% silica.

Several possible equations may be written to describe the reaction between carnotite, salt, and water. The most probable ones are perhaps represented by equations (9), (10), and (11), in which the uranium is converted to the uranate or di-uranate, and the vanadium is converted to the meta- or pyro-vanadate.

$$(9)\ K_2O \cdot 2UO_3 \cdot V_2O_5 + 2NaCl + H_2O \longrightarrow K_2U_2O_7 + 2NaVO_3 + 2HCl$$

$$(10)\ K_2O \cdot 2UO_3 \cdot V_2O_5 + 4NaCl + 2H_2O \longrightarrow K_2U_2O_7 + Na_4V_2O_7 + 4HCl$$

$$(11)\ K_2O \cdot 2UO_3 \cdot V_2O_5 + 4NaCl + 2H_2O \longrightarrow K_2UO_4 + Na_2UO_4 + 2NaVO_3 + 4HCl$$

Experimentally, it was found that addition of 0.020 mole of vanadium in the form of the high grade carnotite resulted in an increase in HCl production of 0.040 mole. Either equation (10) or equation (11) would be in agreement with the experimental data. However, since a number of vanadium compounds have indicated the formation of the meta-vanadate during roasting, it appears that the most probable reaction which the carnotite mineral undergoes is represented by equation (11), in which the uranium is converted to the uranate and the vanadium to the meta-vanadate.

As far as HCl production itself is concerned, these data on the carnotite mineral are of little consequence, because for normal ores, only a small percentage of the HCl produced can be attributed to the mineral. However, the reaction which carnotite undergoes during the roast is of major importance, and any information pertaining to it is of value in other aspects of the roasting treatment.

Other Compounds - Although it has been shown that a number of vanadium compounds are capable of reacting with salt and water to form HCl, the major portion of the HCl evolved during a normal roast has not been accounted for. A 100 gm. sample of Uravan ore contains about 0.02 mole of vanadium, yet reacts with salt and water to form about 0.078 mole of HCl. The free silica, salt, water reaction accounts for about 0.014 mole, leaving about 0.064 mole HCl to be accounted for by vanadium minerals and perhaps other constituents of the ore.

In many ores, a large portion of the vanadium is present as the mineral, Roscoelite, which is a muscovite with some of the aluminum replaced by vanadium. The approximate formula for this mineral is $4H_2O \cdot 2K_2O \cdot 2(Mg \text{ or } Fe)O \cdot 2Al_2O_3 \cdot 3V_2O_3 \cdot 10SiO_2$. A sample of this mineral was not available for testing. However, it seems quite probable that this compound, when heated with sodium chloride, would break down into simple silicates, vanadates, and oxides, and in so doing, would liberate large quantities of HCl. A hypothetical reaction is given by equation (12):

$$(12)\quad 3(4H_2O \cdot 2K_2O \cdot 2MgO \cdot 2Al_2O_3 \cdot 3V_2O_3 \cdot 10SiO_2) + 46NaCl + 11H_2O + 18(O) \longrightarrow$$
$$6K_2SiO_3 + 6MgSiO_3 + 2(3Al_2O_3 \cdot 2SiO_2) + 18NaVO_3 + 14Na_2SiO_3 + 46HCl$$

If such a mineral as Roscoelite were capable of producing HCl during the roast, as speculated above, other complex silicates of a similar type should also serve as a source of HCl, regardless of whether or not vanadium is a constituent. This latter point was tested by subjecting a complex silicate, composed mainly of the mineral, Montmorillonite,

(Mg or Fe)$O \cdot Al_2O_3 \cdot 5SiO_2$, to the standard roasting treatment. No vanadium or uranium was present in this mineral. It was found that 25 gm. of this silicate mineral, when roasted with 9% NaCl, formed 0.027 moles of HCl. This is equivalent to 78 pounds of HCl per ton of mineral.

Summary

The more important pieces of information, which have been gained from this study of HCl production during the salt roast may be summarized as follows:

(1) The roasting conditions usually employed in plant operations are very close to optimum for acid production. No great improvement was indicated by modification of temperature, salt concentration, moisture in the roast atmosphere, bed-depth, or particle size.

(2) The most important single factor upon which the yield of HCl is dependent is the calcite content of the ore. The yield is decreased by 10 pounds per ton for every 1.0% increase in CaO content.

(3) The constituents of the ore which serve as the source of HCl appear to be in the order of their importance (1) vanadium minerals of various types, (2) complex silicates with or without vanadium, and (3) free silica.

The Consumption of Hydrochloric Acid During Leaching

Experimental Methods

As a means of determining the effect of various roasting and leaching conditions on acid requirements, an empirical method was developed by which relative values for acid consumed during the leach treatment could be obtained. This procedure may be described as follows:

A sample of the raw ore, or the salt-roasted, water-leached calcine equivalent to 100 gm. of raw ore, was treated with 200 ml. of standard HCl solution ($\sim$ 5%) with continuous agitation for 2 hours at 80°C. The slurry was filtered while hot and the residue washed thoroughly with water to give a final volume of 500 ml. of filtrate. An aliquot of this solution was titrated potentiometrically with standard NaOH solution. The amount of HCl equivalent to the base required to titrate to an arbitrary pH value, was subtracted from the total amount of HCl to give the relative value for acid consumption.

The arbitrary pH value was set at 1.00 for the original leach solution, because this is approximately the pH at which maximum uranium extraction can be obtained. Since the original solution was diluted by a factor of 2.5 during the filtration, it was necessary to read the back-titration values at a pH of 1.40 which would correspond to a pH of 1.00 in the undiluted leach solution.

The above empirical method was also used in comparing the acid requirements for various ores, although it was recognized that the extreme leaching conditions employed would result in acid requirement

values somewhat higher than would be normally expected in plant operation.

For securing a more meaningful evaluation of the various ores, another method was employed. The minimum quantity of acid required to give near maximum extraction of uranium was determined by conducting a series of leaching tests on each ore. Known quantities of HCl were used in slurries of 50% pulp density at room temperature for 2 hours, and the uranium extraction was determined by analysis of the leach solutions and the residues.

Influence of Roasting Conditions

The data illustrating the effect of various roasting conditions on acid consumption are presented in Tables 28, 29, and 30. It may be observed that the raw ore consumed slightly more acid during leaching than ore roasted without salt. This indicates that certain of the mineral constituents are made more refractory during the 850°C. roast. Ore roasted with sodium chloride and then water-leached prior to the acid-leach, consumes about one-third to one-half as much acid as the raw ore. This indicates that the excess sodium chloride reacts with certain basic constituents to convert them to water-soluble or non-acid consuming compounds.

Although the salt-roasting treatment serves to reduce the acid requirement for processing an ore by a factor of 2 to 3, it may be observed that the conditions of this roasting treatment are not too critical with respect to acid consumption. Temperature appears to be the one variable upon which the acid consumption is most dependent. A roast at

Table 28

General Effect of Roasting Treatment on HCl Consumption

Exp. No.	Ore Treatment	Leaching Acid Concentration (% HCl)	Acid Consumption lbs. HCl/ton ore to give original leach solution of pH: 1.00	1.25
L-481	Raw Ore	5	108	100
V-602	Roasted ore (without salt)	5	91	81
V-604	Salt roasted ore - direct acid leach	5	56	45
V-606	Salt roasted ore - water leach-acid leach	5	42	35
L-479	Raw ore	2	78	68
V-601	Roasted ore (without salt)	2	78	70
V-613	Salt roasted ore - direct acid leach	2	47	37
V-605B	Salt roasted ore - water leach-acid leach	2	41	33

Charge: 100 gm. Uravan (-20 mesh), 9 gm. NaCl in the salt roasts.

Roast: 850°C. for 90 minutes plus heat-up time, bed-depth - 1.2 cm., air flow - 0.2 cu. ft./minute containing 1.0 gm. H_2O/cu. ft.

Leach: 200 ml. of 1.415 N HCl (5%) or 0.563 N HCl (2%) for 2 hours at 80°C. The residue was washed with water to give a final volume of 500 ml. leach solution.

Titration: 200 ml. aliquot was titrated potentiometrically with 1.533 N NaOH. Back-titration volumes were read at pH values of 1.40 and 1.65, which correspond to values of 1.00 and 1.25, respectively, in the original leach solution.

Table 29

Effect of Time and Temperature of Roasting on Acid Consumption

Exp. No.	Roasting Temperature (°C.)	Roasting Time (hrs.)	Acid Consumption lbs. HCl/ton	
			pH = 1.00	pH = 1.25
V-646B	750	1.5	84	74
V-628B	850	1.5	40	32
V-645B	900	1.5	36	28
V-641B	850	0.5	42	35
V-642B	850	2.0	34	24
V-643B	850	3.5	28	20
V-643B	850	6.0	26	17

Remarks: Calcine was water leached prior to the acid treatment. 5% HCl used in all acid leaches. Conditions and method are same as explained in Table 28.

Table 30

Effect of Moisture in Roast Atmosphere and Concentration of NaCl in the Charge on Acid Consumption

Exp. No.	Moisture in Roast Atmosphere (gms. H_2O/100 gm. ore)	% NaCl in Charge	Acid Consumption lbs. HCl/ton	
			pH = 1.00	pH = 1.25
V-505B	none	9	34	26
V-508B	7	9	35	28
V-503B	15	9	34	27
V-506B	68	9	44	36
L-486	15-20	6	52	42
L-434	15-20	9	43	38
L-470	15-20	12	38	27
L-485	15-20	15	38	29

Remarks: Calcine was water leached prior to the acid treatment. 5% HCl used in all acid leaches. Conditions and method are same as explained in Table 28.

750°C. gave consumption values about mid-way between raw ore and ore roasted at 850°C. Higher roasting temperatures had but little effect.

With an increase in time of roasting or NaCl concentration during roasting, the acid consumption decreases slightly. The concentration of moisture in the roast atmosphere seems to have no effect on acid consumption

Influence of Leaching Conditions

In general, it may be noted in Table 31 that the consumption of acid depends in some degree upon the severity of the leaching treatment.

Table 31

Effect of Acid Concentration, Time, and Temperature of Leaching on Acid Consumption

Exp. No.	Ore Treatment	Leaching Conditions % HCl	Temp.	Time (hrs.)	Acid Consumption lbs. HCl/ton pH=1.00	pH=1.25
L-478	Raw ore	2	R.T.	2	66	58
L-480	Raw ore	5	R.T.	2	77	67
L-479	Raw ore	2	80°C.	2	78	68
L-481	Raw ore	5	80°C.	2	108	100
V-629B	Salt roasted-water leached	2	R.T.	2	28	20
V-626B	Salt roasted-water leached	5	R.T.	2	34	25
V-605B	Salt roasted-water leached	2	80°C.	2	41	33
V-607B	Salt roasted-water leached	5	80°C.	1	39	32
V-606B	Salt roasted-water leached	5	80°C.	2	42	35
V-608B	Salt roasted-water leached	5	80°C.	4	46	38

Remarks: Conditions and method are same as explained in Table 28 unless otherwise designated in the Table above.

An increase in temperature from room temperature ($\sim 30^{\circ}C.$) to $80^{\circ}C.$ resulted in a 20 to 30% increase in acid consumption for both raw and salt-roasted ores.

An increase in acid concentration from 2% to 5% HCl resulted in a 20 to 30% increase in acid consumption for raw ores, but a less pronounced increase for the salt-roasted ores, amounting to 10 to 20%.

The time of leaching was less critical than the temperature or the acid concentration during leaching. However, a slight increase in acid consumption with an increase in time of contact was noted.

Comparison of Various Ores

As mentioned previously, the empirical method for determining relative acid requirement values was used in comparing the several types of ore available at this laboratory. The data are contained in Table 32. Again, it should be mentioned that the values reported are only relative, being somewhat higher than would be expected in plant operations because of the extreme leaching conditions used in this method.

It may be observed that the acid requirement is primarily dependent upon the lime content of the ore. However, in the low lime ores, the compounds of magnesium, iron, and aluminum play a more significant role, and thereby lessen the dependence on calcium compounds.

For most of the ores, the acid consumption for the raw ores is about 2 to 3 times that for the salt-roasted ores. However, in the case of the Mineral Mountain-750 ore, which contains 5.7% CaO, the salt-roasted ore required about the same amount of acid as the raw ore. This is

Table 32

A Comparison of Various Types of Ores for Acid Requirements by the Empirical Method*

Type of Ore	% CaO in Head	Raw Ore Consumption (lbs.HCl/ton) Exp. No.	pH = 1.00	pH = 1.25	Salt Roasted Ore Consumption (lbs.HCl/ton) Exp. No.	pH = 1.00	pH = 1.25
Uravan	1.2	L-481	108	100	V-606B	42	35
Wild Steer Mine	1.0	L-507	120	112	V-630B	39	30
Indian Reservation	1.2	L-506	110	94	V-631B	54	43
Cactus Rat-Lot 134	1.6	L-508	140	134	V-632B	40	32
Cactus Rat-Lot 411	2.2	L-509	130	126	L-514B	50	43
Cactus Rat-Lot 254	1.1	L-510	97	90	L-513B	54	46
Rifle	1.6	H-321A	106	98	H-327	48	32
Rico	3.0	H-320A	106	94	H-326	79	67
Mineral Mountain-683	4.0	H-318A	162	154	H-324	82	73
Mineral Mountain-750	5.7	H-319A	199	191	H-325	211	203

Charge: 100 gm. ore (-20 mesh), 9% NaCl in the salt roasts.

Roast: 850°C. for 90 min., plus heat-up, air flow 0.2 cu.ft./ min. (saturated with water at 30°C.), bed-depth - 1.2 cm.

Leach: The roasted material was water leached at 80°C. The acid leach on raw and roasted materials consisted of 200 ml. of 5% HCl for 2 hours at 80°C. Residue was washed with water to give a final volume of 500 ml. leach solution.

Titration: 100 ml. aliquot titrated potentiometrically with 1.533 N NaOH. Back titration volumes were read at pH values of 1.40 and 1.65, which correspond to values of 1.00 and 1.25, respectively, in the original leach solution.

* Explained in body of report.

believed to be due to the much higher aluminum content of the ores in addition to the higher lime content.

For obtaining values more nearly approximating absolute acid requirements in plant operation, the minimum acid requirement method described previously was used. Each ore was tested by subjecting identical samples to a leaching treatment in which the only variable was the amount of HCl used in the leach solution. The percentage uranium extracted with the varying quantities of HCl was determined by analysis of the leach solutions and the residues.

The data obtained by this method are presented graphically in Figures 9 through 14, in which the percentage uranium extracted is plotted against the pounds of HCl per ton of ore used in the leach solutions. The data are summarized in terms of minimum acid requirements for each ore in Table 33.

Table 33

Minimum Acid Requirements for Various Ores

Type of Ore	Lime Content	Minimum Acid Requirement for Leaching lbs. HCl/ton
Uravan	1.2	20
Wild Steer	1.0	40
Cactus Rat-411	2.2	30
Rico	3.0	40
Mineral Mountain-683	4.0	50
Mineral Mountain-684	5.7	150

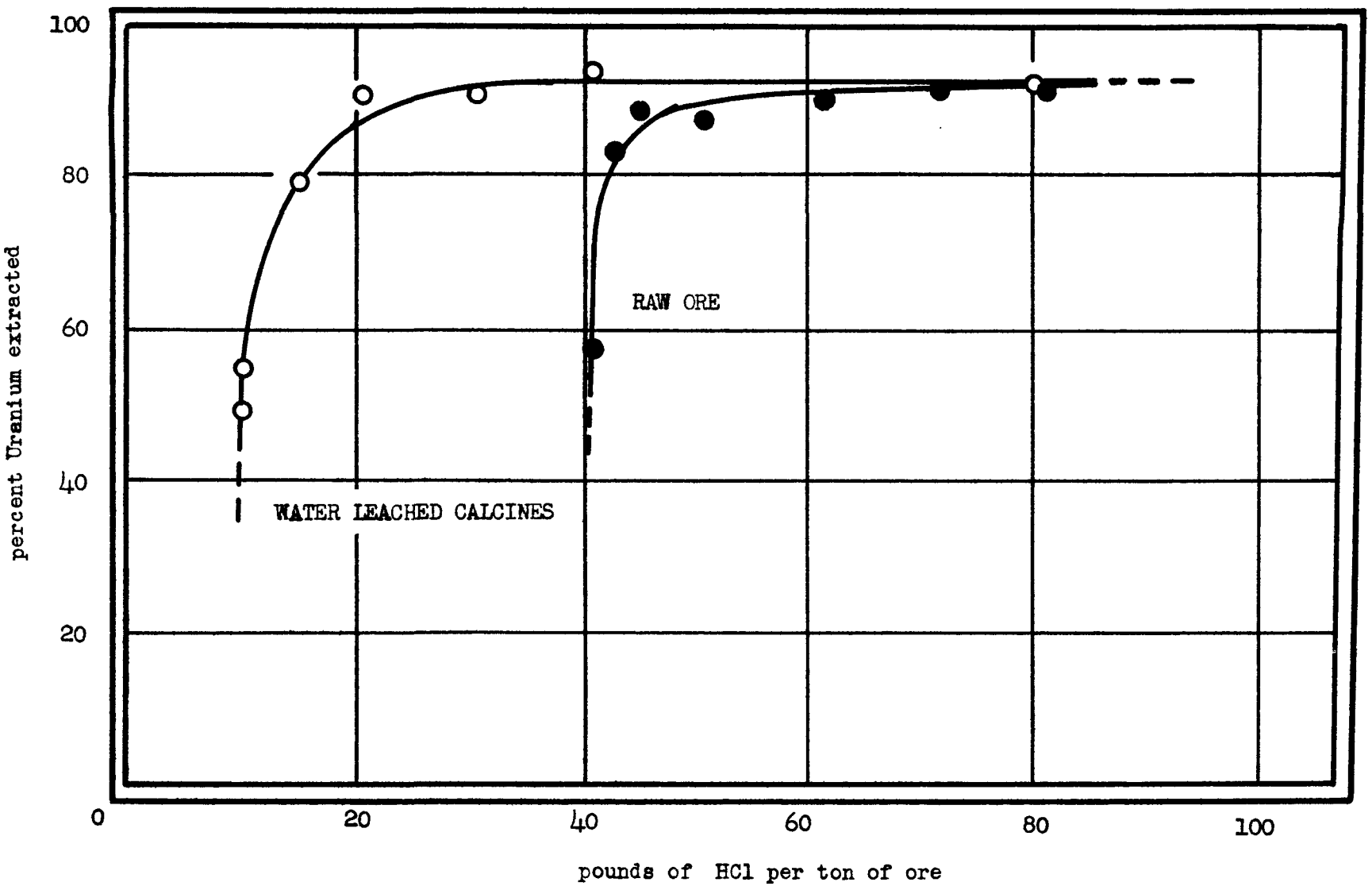


FIGURE 9 - MINIMUM ACID REQUIREMENTS FOR URAVAN ORE

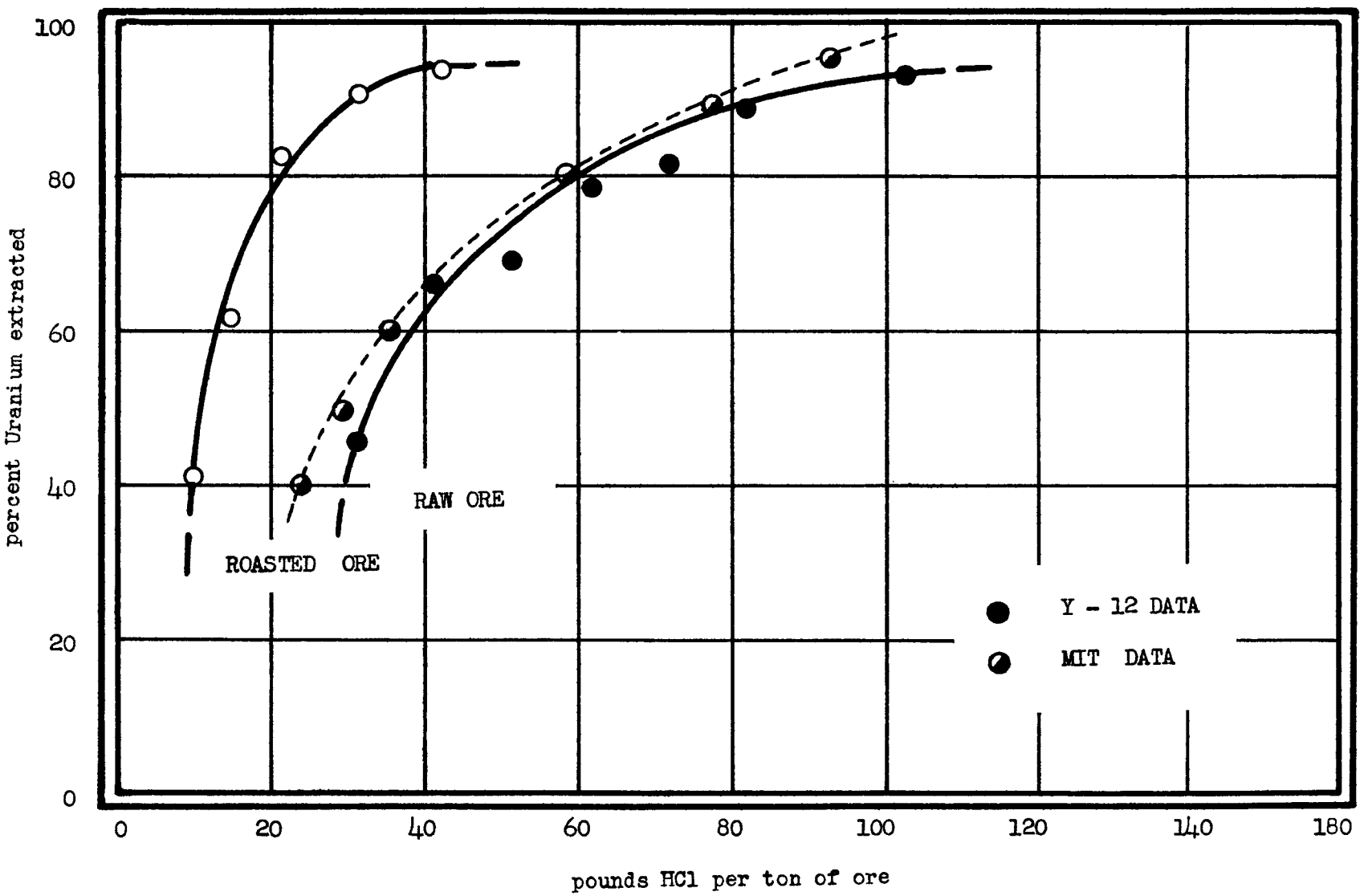


FIGURE 10 - MINIMUM ACID REQUIREMENTS FOR WILD STEER ORE

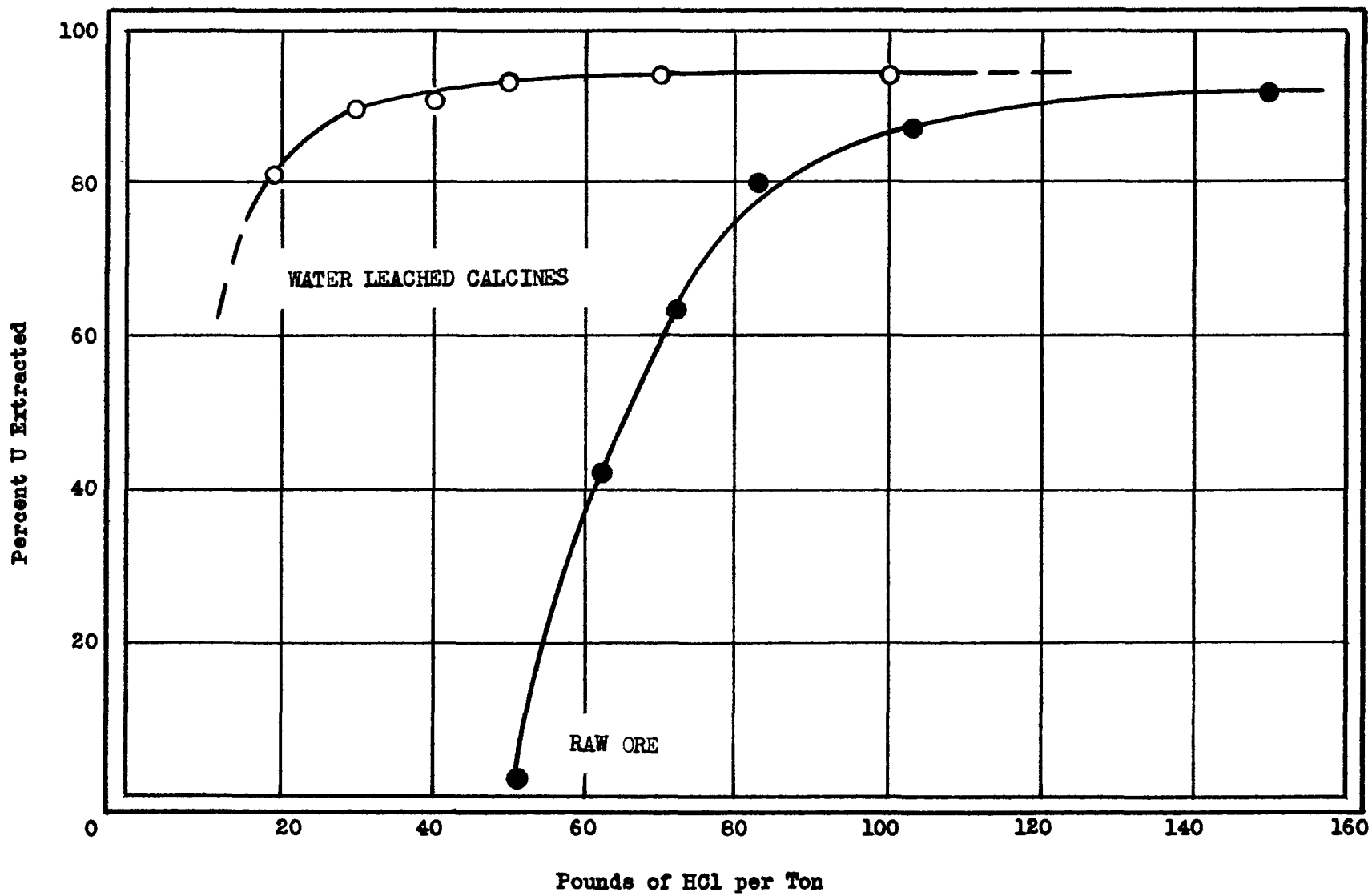


FIGURE 11 - MINIMUM ACID REQUIREMENTS FOR CACTUS RAT, LOT 411, ORE

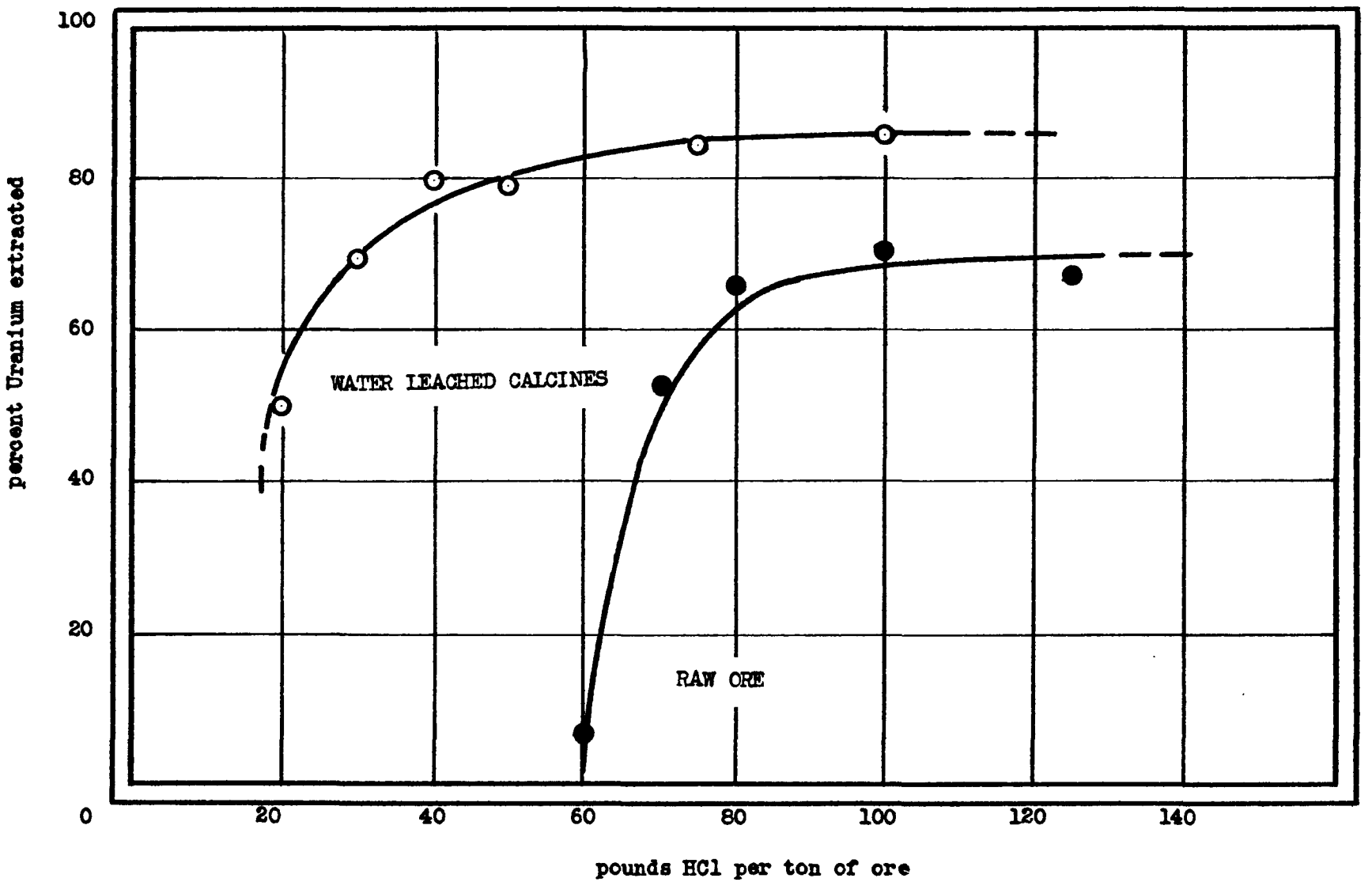


FIGURE 12 - MINIMUM ACID REQUIREMENTS FOR RICO ORE

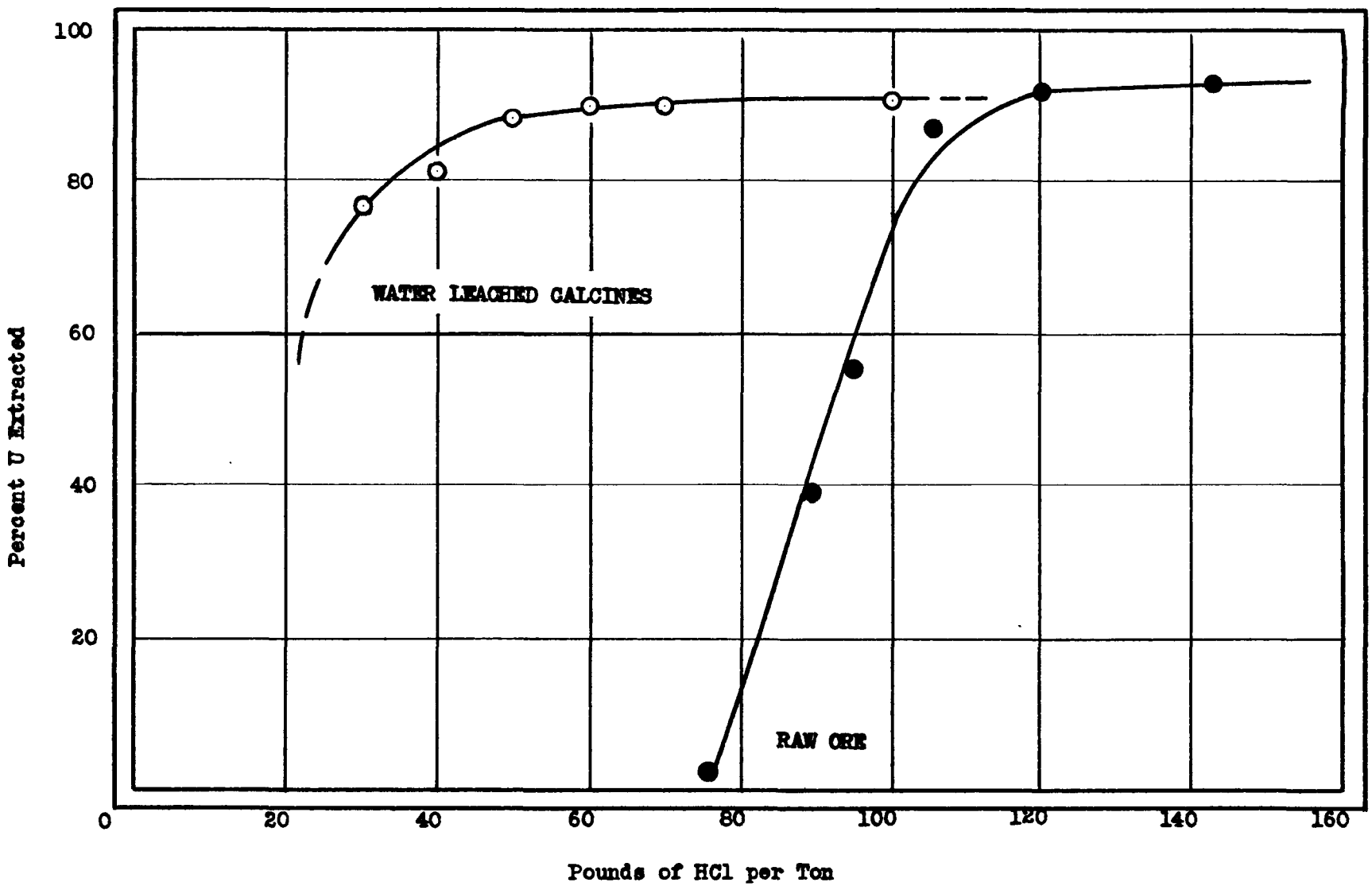


FIGURE 13 - MINIMUM ACID REQUIREMENTS FOR MINERAL MOUNTAIN, LOT 683, ORE

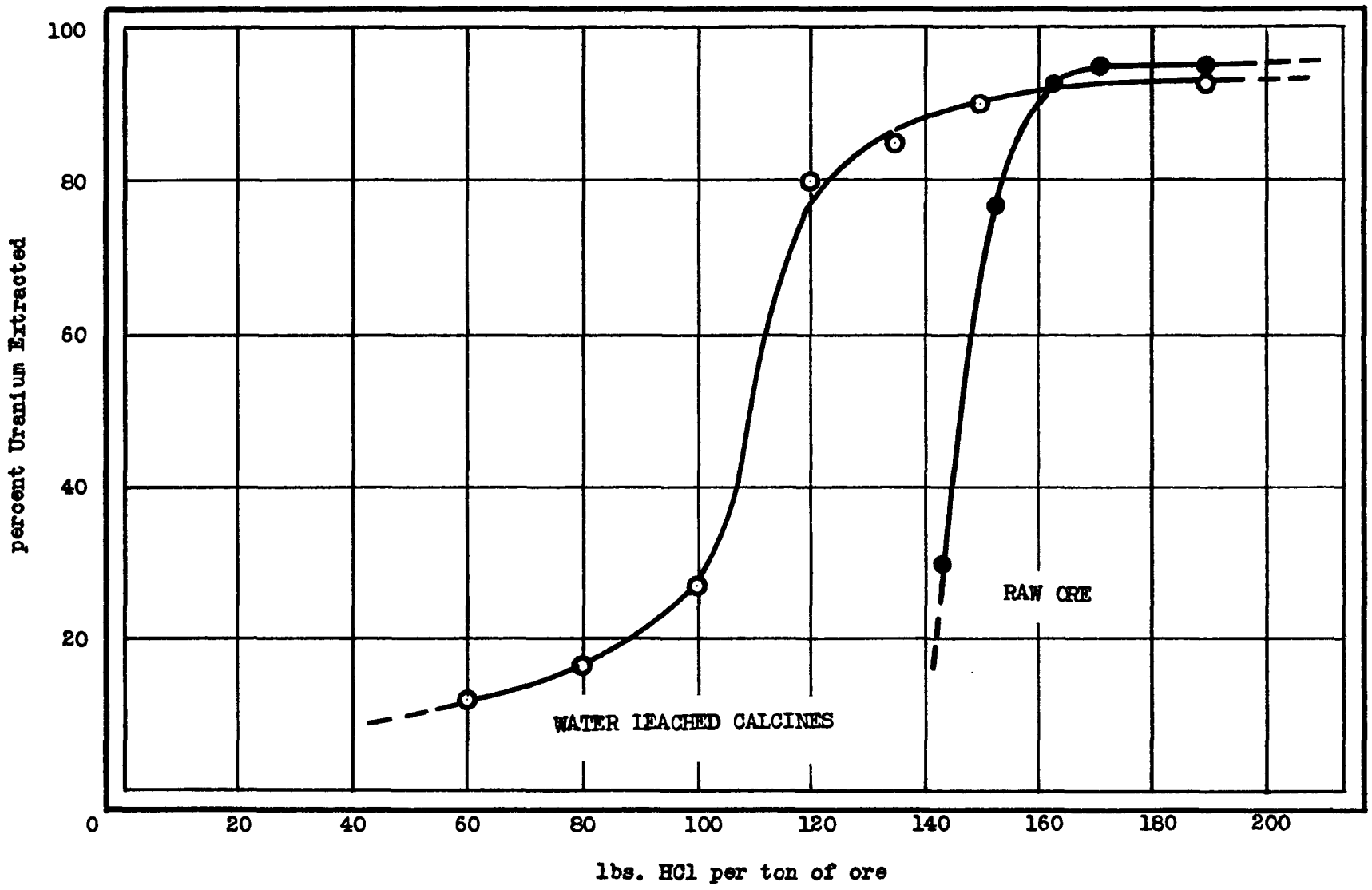


FIGURE 14 - MINIMUM ACID REQUIREMENTS FOR MINERAL MOUNTAIN-750

Again, it is evident that the acid requirement during leaching is primarily dependent upon the lime content of the ore. However, this property cannot be correlated with lime content of the ore as closely as can the HCl production (Table 33). The basic mineral constituents other than CaO were shown to exert little, if any, effect on HCl production, but all contribute appreciably to the acid consumption during leaching.

The Over-all Influence of Calcite on the Acid Process

Introduction

It has been shown experimentally (see previous sections) that other constituents of the carnotite ores have little effect on the acid process, but the calcite concentration is such an important variable that a summary of its over-all effect on the process seems desirable. As shown previously, the calcite in the ore demonstrates its effect in two ways.

First: with increasing amounts of calcite (usually expressed as CaO) in the ore, decreasing quantities of vanadium are extracted by the water leach. This phenomenon is undoubtedly caused by the conversion of vanadium minerals, during the roast, to the water-insoluble calcium vanadate rather than to the water-soluble sodium vanadate.

Second: the presence of increasing quantities of calcite in the ore effects a decrease in the amount of HCl produced during roasting and also requires an increase in the amount of HCl used in the leaching of the resultant calcines.

At least the first of these deleterious effects from the calcite contents has been recognized for some time and, as mentioned before, any trouble from this source has been avoided by the simple expedient of refusing to buy any but the low calcite materials. However, large bodies of ore in the Colorado Plateau are rather high in lime and, eventually, these sources must be processed.

By blending high lime and low lime ores, a "head" material of any desired CaO content can be achieved. If the lime tolerance of the acid process is known, it should be possible to process considerable quantities of the high lime ores in these plants by using blended ores rather than arbitrarily limiting the buying program to only the low lime materials.

Calcite Limit Imposed by Recoveries

Uranium recoveries from high lime ores are satisfactory. To gain satisfactory extractions of vanadium into the water leach solutions, however, the calcite content of the ore should not exceed about 2.5% as CaO (see Table 33 above).

Calcite Limit Imposed by HCl Balance

For most efficient operation of the acid process, the HCl production should be, in all cases, equal to or slightly greater than the quantities which will be needed in the leaching operations so that extra acid does not have to be purchased and transported to the mill site. The effect of CaO on HCl production has been presented in Table 25, and

the effect of HCl consumption in Table 33. A comparison of the two sets of data is given below in Table 34. It may be concluded that the quantities of acid produced by the acid process will not be as great as the quantities required for leaching if the ores being processed contain more than 2.5 to 3% CaO.

Table 34

Influence of Calcite Content of Ore on Hydrochloric Acid Balance

Type of Ore	Lime Content	Minimum Acid Requirement for Leaching (lbs. HCl/ton)	HCl Production during Roasting (lbs. HCl/ton)
Uravan	1.2	20	57
Wild Steer	1.0	40	61
Cactus Rat-411	2.2	30	--
Rico	3.0	40	42
Mineral Mountain-683	4.0	50	36
Mineral Mountain-750	5.7	150	17

Sulfate Roasts of High Lime Ores

From the information presented above, it is apparent that the acid process, as currently operated, is hardly a satisfactory process for greater than 2.5 to 3% in CaO. Other methods for use in other plants have been developed for application to these materials.

It is conceivable, however, that because of transportation costs

or other reasons, it may be advantageous at times to handle some of these high lime ores in the acid process plants. A few experimental investigations have been directed toward this possibility.

In Table 35, results are presented from the tests in which varying quantities of H_2SO_4 were added to a Mineral Mountain, high-lime ore, prior to roasting. With increasing additions of H_2SO_4, increasing quantities of vanadium were obtained in the water leach. The H_2SO_4 inhibits the formation of calcium vanadates (forming $CaSO_4$ instead) and allows increased quantities of vanadium to appear in the water leach as water-soluble $NaVO_3$. Upon adding H_2SO_4 equivalent to 3/4 of the CaO content, the vanadium extractions reached the normal level.

For this particular ore (5.7% CaO), the H_2SO_4 requirement is rather high. This requirement would be less with ores somewhat lower in CaO content. The H_2SO_4 additions cause an increase, however, in HCl production (and, of course, a decrease in consumption). Conceivably, arrangements could be made to re-employ the acid that has been regained in this manner.

Another advantage of the sulfuric acid roasts is the improvement in filtrability of the high-lime calcines. Formation of silica gels made it difficult to filter high-lime calcines after a normal roasting treatment. This effect was not observed in any of the sulfating roasts.

It seems possible that, if necessary, certain modifications of the acid process could be applied to ores higher in lime at some increase in processing costs. Since some of the additional acid required is re-

Table 35

High Lime Ores Roasted with H_2SO_4

Exp. No.	H_2SO_4 Added (lbs./ton of Ore)	CaO Neutralized (%)	Water Soluble V (%)	HCl Required for Leaching (lbs/ton)	HCl Produced In Roast (lbs/ton)
H-313	0	0	1	150	17
L-604	65	35	17	90	-
L-603	100	50	42	60	66
L-602	150	75	72	50	-
L-601	200	100	72	35	100

Roast: 100 gms. of -20 mesh Mineral Mountain-750 ore (5.7% CaO) plus 9% NaCl roasted at 850°C. for 1.5 hours (plus heat-up) with a .24 CFM dry air flow over a 1/4" bed.

H_2O Leach: 200 ml. of H_2O per 100 gms. ore for 2 hours at 80°C.

gained in the process, it is probable that the increase in cost would not be great with moderate, high-lime materials.

Precipitation of Uranium and Vanadium from Leach Liquors

As shown in Appendix B, vanadium is precipitated from the water leach solution as "red-cake" (probably a sodium polyvanadate) by a simple process which involves only the addition of sulfuric acid. The precipitation reactions for removing uranium and vanadium from the acid liquors are, on the other hand, rather complicated. Although the final recoveries of both the uranium and vanadium are fairly quantitative, the procedure requires considerable handling of the solution, with a number of troublesome filtrations. In addition, since the solution is adjusted back and forth between the acid and basic sides several times, the reagent usage is quite large.

It has been the opinion of the plant operators that a better answer to the precipitation chemistry must exist, and that an improvement in this operation would mean a significant boost to the process as a whole. Therefore, little time has been spent at Y-12 in investigation of the solution process as it is now being applied, but rather the work has been directed toward the development of an entirely new and better method for gaining the uranium and vanadium values.

It is believed that this aim has been accomplished by a process in which the uranium is first obtained as a precipitate of uranous phosphate and the vanadium is gained from the residual liquors as a precipitate of

vanadic phosphate. A complete discussion of this process, as well as other solution chemistry studies, will be given in later papers.

Summary

The investigation of the "acid process" as applied to various carnotite and roscoelite ores has been completed. The reactions of these ores to the process have been considered from the standpoint of (1) the percentages of uranium and vanadium recovered, (2) the quantities of HCl produced, and (3) the amounts of HCl consumed. Optimum conditions have been determined and those ores to which the process may be applied with proficiency are recognized.

The roasting and leaching steps in the process are not exceedingly critical, and within a fairly wide range of conditions, the acid process is a rather efficient one for obtaining uranium and vanadium from low-lime, high-vanadium ores.

The factor imposing the major limitation on the process is the concentration of CaO which may be tolerated in the feed material. To attain optimum recoveries and to attain a production of acid equivalent to the amount used, the CaO content should be limited to a concentration of about 2.5%. With some modification of the process (sulfate roasting) and with some increase in processing costs, it may be possible to process ores of somewhat higher lime content.

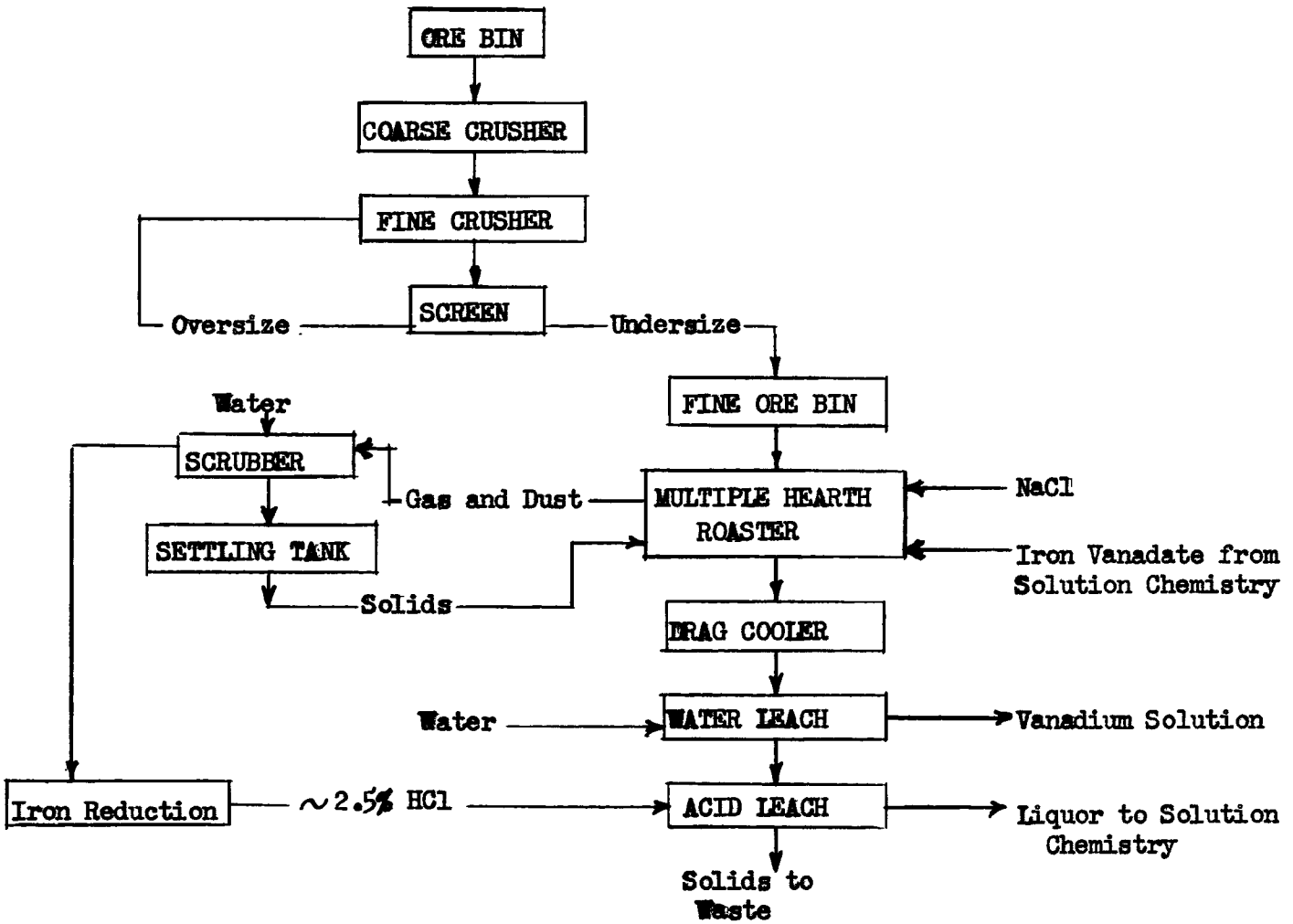
Good recoveries of uranium and vanadium are obtained by present plant precipitation methods but the processes are complicated and costly.

It is believed that the major over-all improvements in the process can be made by replacing the present solution chemistry methods. A process developed for this purpose will be described in a later paper.

APPENDIX A

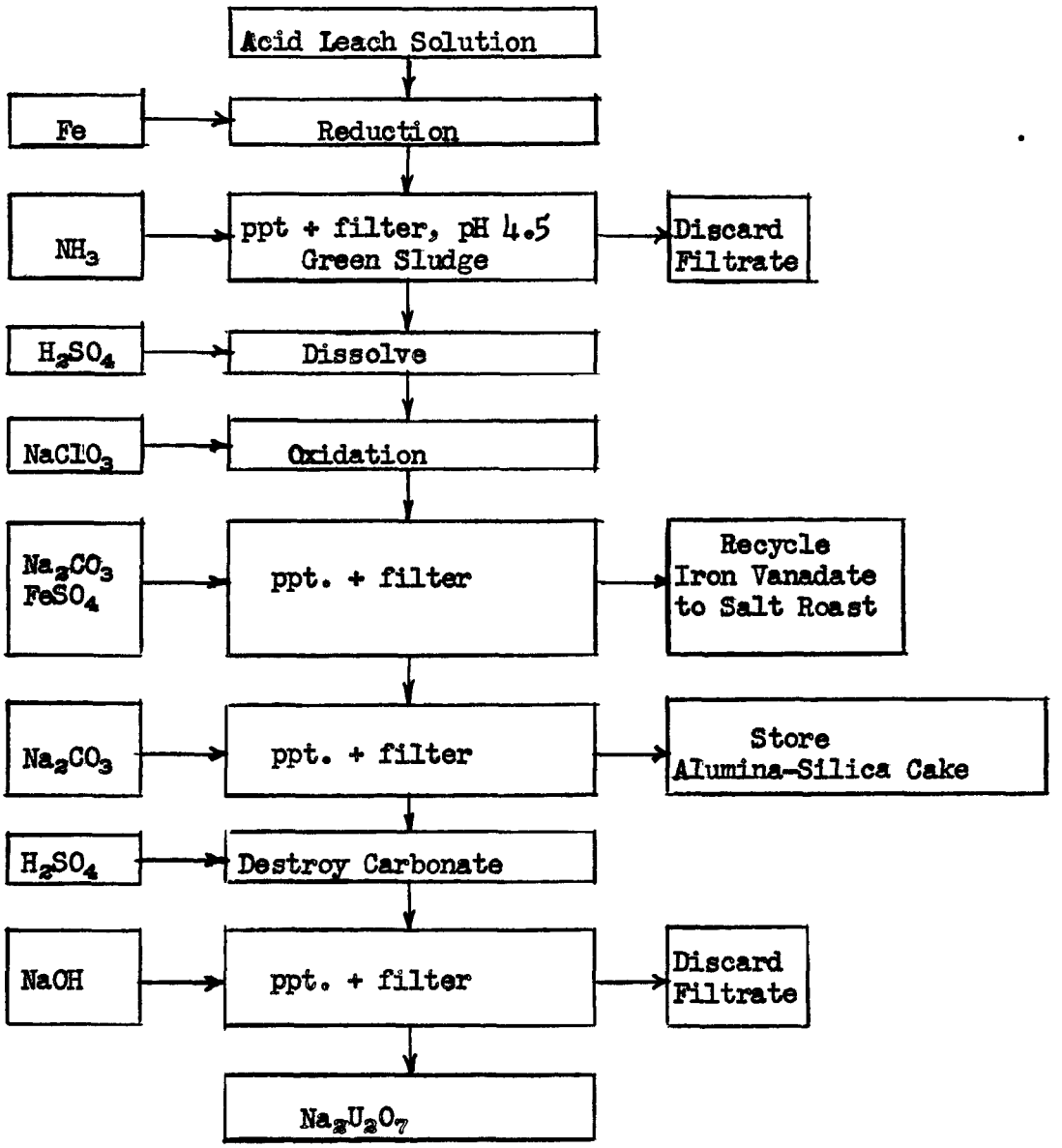
List of Reports Submitted Since the Beginning of the Western Ore Studies

1. Monthly Progress Report for July, 1948 ------- Y-211
2. Monthly Progress Report for August, 1948 ----- Y-229
3. Monthly Progress Report for September, 1948 -- Y-256
4. Monthly Progress Report for October, 1948 ---- Y-277
5. Monthly Progress Report for November, 1948 --- Y-294
6. Monthly Progress Report for December, 1948 --- Y-312
7. Monthly Progress Report for January, 1949 ---- Y-335
8. Monthly Progress Report for February, 1949 --- Y-360
9. Monthly Progress Report for March, 1949 ------ Y-375
10. Monthly Progress Report for April, 1949 ------ Y-396
11. Monthly Progress Report for May, 1949 -------- Y-416
12. Monthly Progress Report for June, 1949 ------- Y-440
13. Monthly Progress Report for July, 1949 ------- Y-458



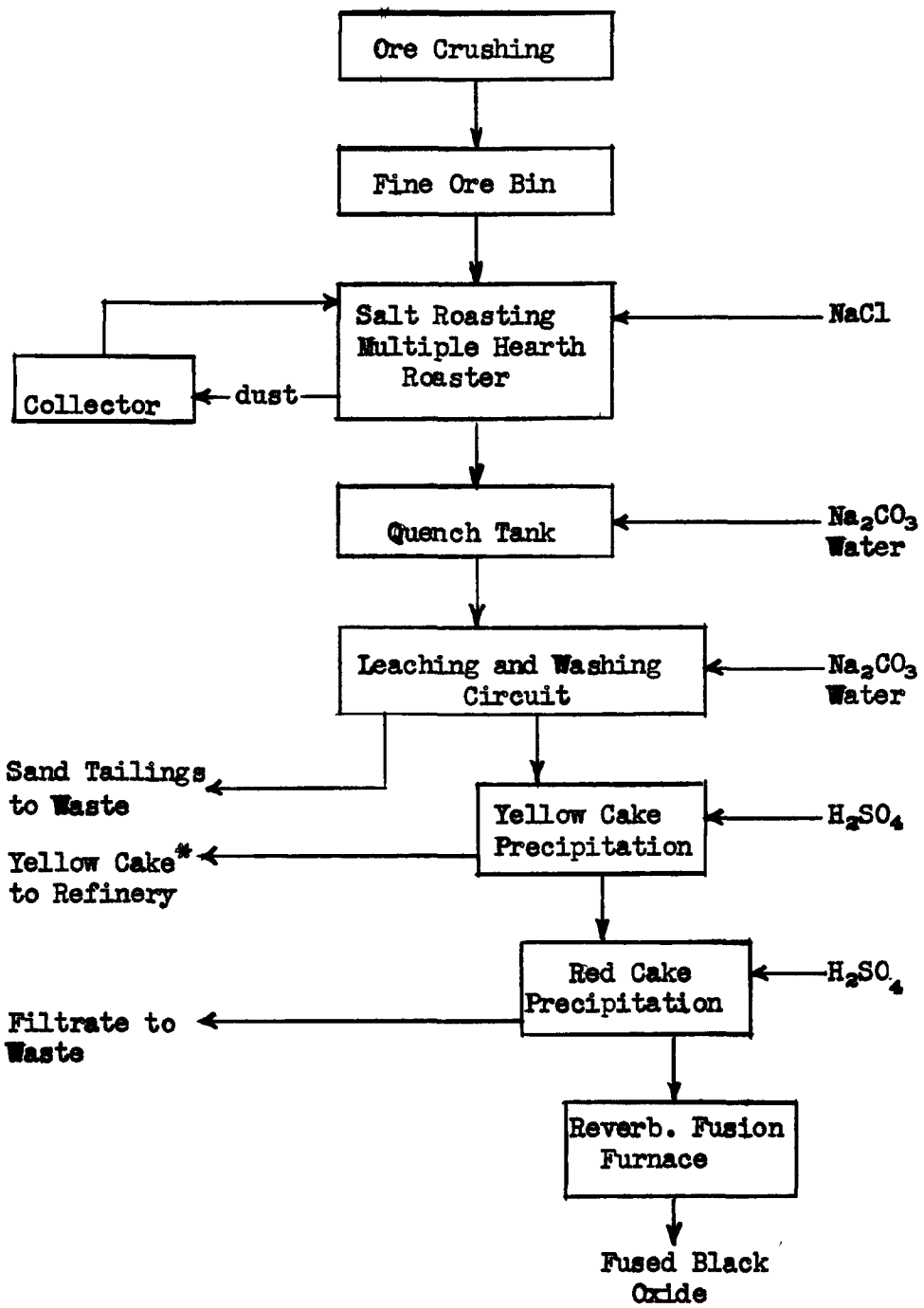
APPENDIX B. Flowsheet of Rifle Process

APPENDIX B. (continued)



APPENDIX C

Simplified Flowsheet of Carbonate Process



* In Refinery, the yellow cake (a uranyl vanadate) is fused with Na_2CO_3 and sawdust to form UO_2 and a water soluble sodium vanadate which is recycled to the red cake pptn.

PART II. DIRECT ACID-LEACHING OF WESTERN URANIUM-BEARING ORES

Introduction

By direct treatments with dilute acid solutions, almost all of the contained uranium can be extracted from the carnotite (and roscoelite) ores that are available at this laboratory (for ores treated in this manner, see Table 4, page 118). Due to reasons discussed later, considerable variations in the vanadium extractions are realized from ore to ore. With the carnotite samples, these extractions have ranged from about 20 to 80 percent. With the roscoelite ores, only 1 to 5 percent of the total vanadium was solubilized.

The amounts of acid which are consumed in leaching the different raw ores are dependent upon the concentration of soluble bases - the most important of which is calcite. In turn, the extent of dissolution of the bases is affected somewhat by the acid concentration and temperature of the leach solutions.

Experimental Procedure

Chemical compositions of the ores used in the direct leaching experiments have been presented previously in Table 1 (Description of Ore Samples, page 9). The procedure used for the direct leaching tests may be described, in general, as follows: 100 gm. samples of the raw ore batches were treated with the acid solutions in 1 liter Berzelius beakers. Agitation was supplied by motor-driven stirrers and increased temperatures were obtained by use of a constant temperature bath.

The leach slurries were filtered on Buchner type funnels and the residues were, in all cases, washed thoroughly with water. In many of the tests, two leachings were made in sequence to make certain that all of the soluble uranium had been gained.

The acid liquors and the ore tailings were analyzed for their uranium and vanadium content. Percentage recoveries, as calculated for each experiment, were based on the total uranium or vanadium that was accounted for in the particular test; thus, nearly eliminating any variations due to sampling.

Experimental Results

Effect of Ore Mesh Size

Direct leaching tests, made on Uravan ore samples of different mesh size, are presented below in Table 1. High extractions of uranium were obtained with all the ore batches (ranging from -4 to -100 mesh), though it is indicated that these high extractions are more consistent when using material crushed to somewhere in the range of 20 mesh or below. Also, a small additional advantage in extraction was gained by grinding of the ore to very fine particle size, i.e., -80 or -100 mesh.

It was noticed during preparation of finer particle size samples that the Uravan ore could be quickly and easily crushed to pass a 60-mesh sieve. Only little difficulty was experienced in crushing the ore to pass an 80-mesh sieve whereas extended ball-milling periods were necessary for preparation of minus 100-mesh samples. Apparently, the average sand

grain size for the Uravan ore is of the order of 80 mesh.

With this in mind, it is interesting to re-examine the data in Table 1. From tests B-18 and B-19, it may be observed that extractions are not increased by further crushing once the grain size of the ore has been attained. In other words, a measure of the total "available" uranium may be obtained by acid leaching an ore that has been crushed to the point of total liberation.

Table 1

Effect of Mesh Size on Direct Leaching of Raw Carnotite Ore

Exp. No.	Ore Mesh	1st Leach		2nd Leach		Tails			
		U	V	U	V	U		V	
		% of Total	% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
B-15	-4	96	42	0.5	7	0.004	4.0	0.485	51
B-16	-8	93	36	1.0	6	0.015	6.0	0.525	58
L-365	-20	97	42	0.5	11	0.004	2.5	0.445	47
B-17	-60	97	32	0.5	13	0.004	2.5	0.520	55
B-18	-80	97	36	1.5	12	0.002	1.5	0.500	52
B-19	-100	98	37	0.4	10	0.002	1.5	0.495	53

Average Analyses of the head samples: U_3O_8 = 0.15%; V_2O_5 = 1.7%.

Ore Sample: 100 g. of raw Uravan ore.

Acid Leach: 200 ml. of 5% HCl agitated 4 hours at 80°C.

Effect of Leaching Temperature and Acid Concentration

Data from direct leaching experiments at 80°C. with raw Uravan ore, using different concentrations of HCl and H_2SO_4, for various times, are presented in Table 2. Data from comparative experiments, made at room temperatures, are given in Table 3. Second leaches were made in all cases as a further check on the effectiveness of a single leach.

At 80°C., 1% acid solutions, under the conditions of the experiments, were not sufficient for maximum uranium removal by a single leach. Two percent solutions were nearly sufficient with perhaps a small advantage being gained with 5% solutions (practically no uranium in the second leach). Further increases in the acid strength (up to 20%) gave no observable improvement. Also, only small gains in extraction were obtained by increasing the leach period from 1/2 to 4 hours.

At room temperature, the recoveries by a single leach were slightly lower, in general, than those obtained at 80°C. The effect of increased acid strength and increased leaching times were somewhat more pronounced at this temperature.

As was expected, the vanadium extractions by the direct acid treatments were quite low and varied considerably with the time, temperature, and concentration of the leach. It may be simply stated that near maximum extraction of the uranium (95%) could be attained with a simultaneous extraction of only about 20% of the vanadium values.

Other experiments which more clearly show the effect of acid concentration on uranium extraction are presented in a following section

Table 2

Direct Leaching of Raw Carnotite

80°C. Leaches

Exp. No.	% Acid	Leach Time (hrs.)	1st Leach U % of Total	1st Leach V % of Total	2nd Leach U % of Total	2nd Leach V % of Total	Tails U % of Wt.	Tails U % of Total	Tails V % of Wt.	Tails V % of Total
L-350	1% H_2SO_4	1	90	7	3	8	0.009	7	0.790	85
L-351	1% H_2SO_4	4	90	12	6	12	0.006	4	0.560	76
L-352	5% H_2SO_4	1	95	30	0.7	5	0.006	4	0.550	65
L-353	5% H_2SO_4	4	96	39	0.4	10	0.005	4	0.510	51
L-355	20% H_2SO_4	4	96	51	0.3	9	0.005	4	0.400	40
L-363	1% HCl	4	90	-	5	-	0.006	5	-	-
S-372	2% HCl	2	93	27	2	8	0.006	5	0.560	65
S-375	5% HCl	1/2	95	22	0.7	7	0.005	4	0.565	71
L-364	5% HCl	1	95	22	1.5	9	0.005	4	0.665	69
L-365	5% HCl	4	97	42	0.4	11	0.005	3	0.445	47
L-367	20% HCl	4	96	-	0.3	-	0.005	5	-	-

Ore Sample: 100 gms. of Uravan ore ground to minus 20 mesh.

Leach Description: 300 ml. of leach solution per 100 gms. ore at 80°C.

Table 3

Direct Leaching of Raw Carnotite

Room Temperature Leaches

Exp. No.	% Acid	Leach Time (hrs.)	1st Leach		2nd Leach		Tails			
			U	V	U	V	U		V	
			% of Total	% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
S-340	1% HCl	2	89	8	6	4	0.006	5	0.825	88
S-342	1% HCl	8	91	-	5	2	0.005	4	-	-
S-344	2% HCl	2	93	12	3	2	0.005	4	0.825	86
S-347	2% HCl	24	94	18	1.5	8	0.005	4	0.665	75
S-348	5% HCl	2	94	14	2	2	0.005	4	0.775	84
S-350	5% HCl	8	95	14	1	3	0.005	4	0.900	83
S-356	20% HCl	2	97	18	0.5	4	0.003	3	0.810	78
S-359	20% HCl	24	97	30	0.2	6	0.004	3	0.670	64

Ore Sample: 100 gms. of Uravan ore ground to minus 20 mesh.

Leach Description: 300 ml. of leach solution per 100 gms. ore at room temperature.

entitled "Minimum Acid Requirements for Raw Ore Leaching".

Direct Acid Leaching of Several Ores

Uranium and vanadium extraction data from direct treatments of various ores with different strength acid solutions are presented in Table 4. As anticipated from the work with Uravan ore, high recoveries of uranium were obtained from all the carnotite type ores provided sufficient acid was present in the leach solution. Due to lower concentrations in the head samples, the extractions of uranium from the roscoelite ores were somewhat lower on a percentage basis. However, since the tailings contained the same low level of uranium concentration as obtained from the carnotite ores, i.e., about 0.007%, these extractions must be considered as satisfactory.

The tests in Table 4 serve very well in showing the differences in vanadium extractions that are obtained upon treating different ores in a similar manner. A 5% HCl leach extracted about 80% of the vanadium from the Indian Reservation and Wild Steer Mine ores. With Uravan ore, the extractions were only about 20%, and with the roscoelite ores (Rico and Rifle), the vanadium extractions were 2% and 11%, respectively.

These differences in extractions arise from the fact that vanadium is contained by the ores in several mineral forms. In the roscoelite ores, the vanadium is present, almost entirely, as an acid-insoluble vanadium mica (roscoelite). In the carnotite ores, the vanadium may be present as the acid-soluble vanadyl-vanadates and calcium vanadates, as well as the vanadium micas.

Table 4

Direct Leaching of Raw Carnotite Ores

Exp. No.	Source of Ore	HCl (%)	Extractions				Tails			
			1st Acid Leach		2nd Acid Leach					
			U	V	U	V	U		V	
			% of Total	% of Total	% of Total	% of Total	% of Wt.	% of Total	% of Wt.	% of Total
S-372	Uravan	2	93	27	2	8	0.006	5	0.560	65
L-365	Uravan	5	97	42	0.4	11	0.005	2.5	0.445	47
H-189	Wild Steer	2	94	60	3	17	0.008	3	0.455	23
H-190	Wild Steer	5	97	79	0.3	6	0.008	3	0.300	15
H-183	Indian Reservation	2	94	38	6	26	0.004	0.2	0.510	36
H-184	Indian Reservation	5	99.5	74	0.3	14	0.001	0.1	0.160	12
H-202	Cactus Rat-Lot 254	2	89	42	4	9	0.007	7	0.135	49
H-205	Cactus Rat-Lot 254	5	97	52	0.2	7	0.003	3	0.114	41
H-203	Cactus Rat-Lot 134	2	89	33	6	21	0.007	5	0.340	46
H-206	Cactus Rat-Lot 134	5	94	51	2	17	0.005	4	0.245	32
H-204	Cactus Rat-Lot 411	2	67	23	24	23	0.006	9	0.415	54
H-207	Cactus Rat-Lot 411	5	96	57	0.1	13	0.003	4	0.240	30
H-318	Mineral Mountain-683	5	94	30	1	2	0.007	5	0.530	68
H-319	Mineral Mountain-750	5	94	16	2	1	0.007	4	0.720	83
H-352	Rifle	5	94	11	-	-	0.002	6	1.020	89
H-353	Rico	5	85	2	-	-	0.008	15	1.250	98

Leach Conditions: 200 ml. of leach solution per 100 grams sample of ore (-20 mesh) for 2 hours at 80°C.

Previous workers have tried to develop processes in which the uranium could be dissolved in an acid solution, and the vanadium left behind for stockpiling and future processing. These efforts have met with little success. Although such a process might be worked out satisfactorily to fit a particular ore body, it would hardly be universal in application.

Rates of Dissolution

Uranium is rapidly dissolved from carnotite ores by leach solutions of moderate acid strength. To determine the dissolution rates for uranium, and also vanadium, tests were made in the following manner: Two-hundred grams of raw Uravan ore was agitated with 400 ml. of HCl solution in a constant temperature bath at 80°C. (HCl solution preheated to 80°C. before mixing). Samples of the ore were "thiefed" from the mixture at various time intervals and were quickly filtered and washed on a large Buchner funnel (time for this operation equaled about one minute). Duplicate determinations of uranium and vanadium were obtained on each sample.

The data, as presented in Table 5, show that essentially all of the acid-soluble uranium is extracted almost immediately by the dilute acid solutions.

A fair portion of the acid-soluble vanadium is also rapidly taken up by the acid leach, but measurable additions in extractions are gained by increased leaching times and increased acid strengths.

Table 5

Dissolution Rate of Uranium and Vanadium

in Acid Leach of Raw Ore

Run No.	Conc. HCl (%)	Time (min.)	Tails U (%)	Tails V (%)
M-215-SA	2	5	0.025	0.50
M-215-SB	2	10	0.016	0.59
M-215-SC	2	20	0.007	0.57
M-215-SD	2	30	0.008	0.47
M-215-SE	2	90	0.007	0.44
M-215-SF	2	240	0.006	0.44
M-218-SA	5	5	0.010	0.52
M-218-SB	5	10	0.008	0.57
M-218-SC	5	20	0.008	0.50
M-218-SD	5	30	0.007	0.50
M-218-SE	5	90	0.007	0.45
M-218-SF	5	240	0.007	0.38

Procedure: 200 ml. of leach solution per 100 grams of ore (-20 mesh Uravan) at 80°C.

Nature of "Unavailable" Uranium

Upon referring to the data from direct leaching tests with any of the raw ores (Tables 1, 2, 3, and 4), it may be noted that the uranium content is reduced to a certain low level beyond which further leaching is of no avail. For the several ores studied, this "unavailable" uranium has ranged from 0.001 to 0.008% of the ore weight.

To obtain some information as to the nature of uranium hold-up in these tailings, experiments were conducted with Uravan stockpile ore as follows:

Two 100-gram batches of raw ore (minus 20 and minus 100 mesh) were treated four times with 10% HCl solution for 4 hours at 80°C., and samples of the tails were submitted for analysis. Each batch was then treated for four minutes at room temperature with 24 percent hydrofluoric acid solution (2 ml. of solution per 1 gram of ore), and after filtering and washing, samples were taken again for analyses. The final treatment consisted of another hydrofluoric acid leach carried out in the same manner as the first, analyses also being obtained on the final residues. About 10% of each batch was dissolved by the hydrofluoric acid solutions.

The experimental results in Table 6 show that the uranium contents of the ores after four leachings with 10% acid were no lower than after two leachings with 5% acid. Treatments with HF reduced the uranium content of the -20 mesh tailings from 40 to 20 ppm whereas the -100 mesh tailings (already at 20 ppm) were unaffected.

As concluded previously, the "available" uranium is completely dissolved from a well-crushed, raw ore by a single leach with dilute acid. In addition, it is shown by the data that the small quantity of remaining material is tenaciously and uniformly bound by the silica gangue. For the Uravan ore, the concentration of this "unavailable" uranium is in the order of 20 ppm - a value not too far removed from the average general uranium content of granitic rocks.

Table 6

Experiments with Carnotite Tailings

Exp. No.	Mesh	Tail Analyses					
		After 4 Acid Leachings		After 1 HF Treatment		After 2 HF Treatments	
		% U	% V	% U	% V	% U	% V
M-208	-20	0.004	0.46	0.003	0.12	0.003	0.02
		0.004	0.46	0.002	0.14	0.002	0.03
M-210	-100	0.002	0.42	0.002	0.08	0.002	0.02
		0.002	0.46	0.002	0.08	0.001	0.05

Minimum Acid Requirements for Raw Ore Leaching

The theoretical quantity of acid required for reacting only with the carnotite mineral in an ore is very small. Fairly large amounts of acid are neutralized, however, by other basic constituents in the ore, e.g., $CaCO_3$, $MgCO_3$, and Al_2O_3.

To determine the "absolute" quantities of acid that must be used to obtain nearly complete solubilization of uranium from several raw ores, tests were conducted in the following manner: 800 gms. of minus 20 mesh ore were riffled into 8 equal samples. Each 100 gm. portion was then agitated with 100 ml. of solution (containing increasing quantities of HCl) for 2 hours at room temperature. After filtration and washing, uranium analyses were made on the leach solutions and on the tailings.

Six different ores were studied in this manner and a graphical presentation of the data is made in Figure 1. From these extraction-consumption plots, the minimum acid requirements for each ore may be deter-

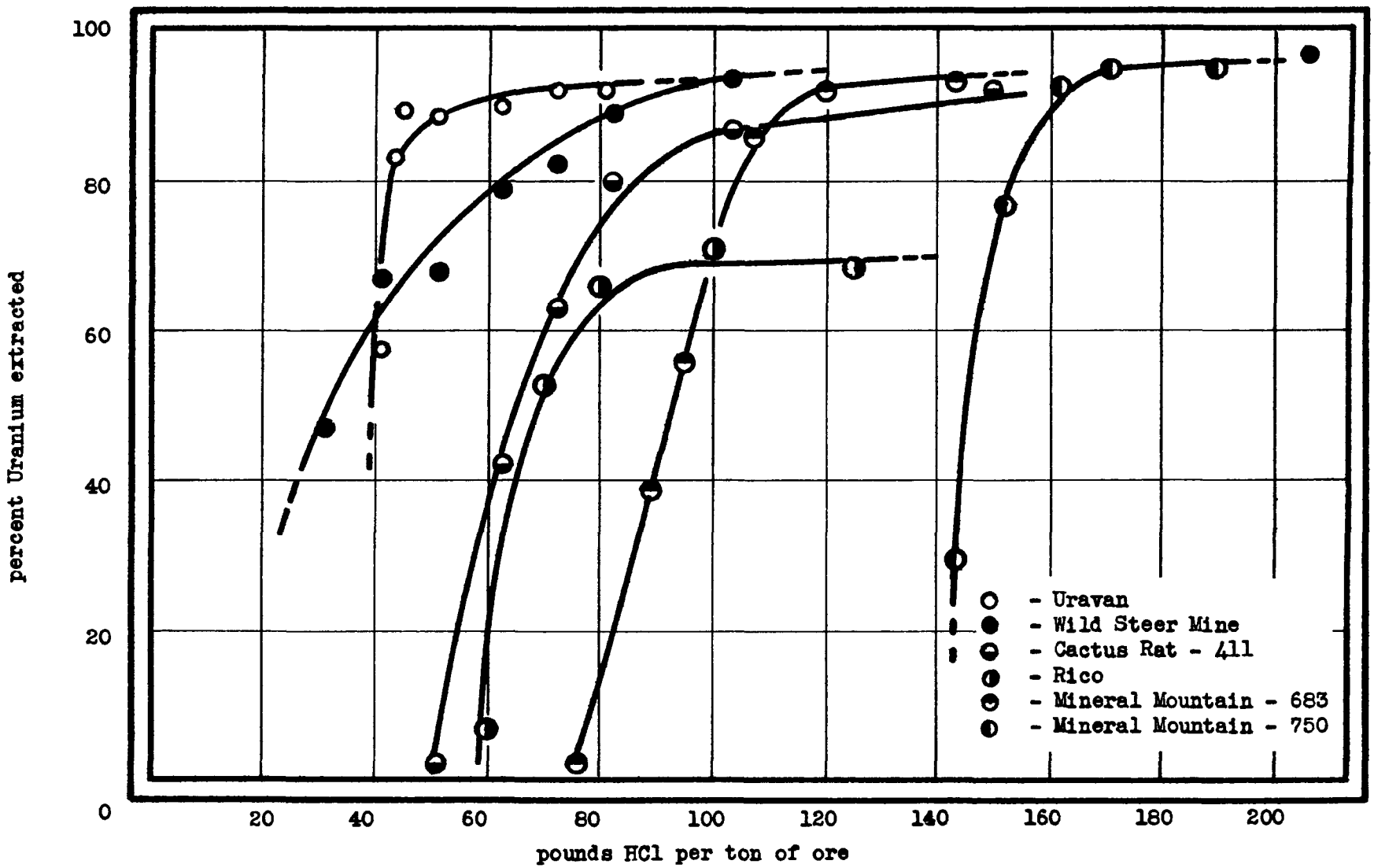


Figure 1. The Minimum Acid Requirements for the Direct Leaching of Various Raw Ores.

mined. A tabulation of these values is given in Table 7.

Table 7

Minimum Acid Requirements for Various Ores

Type of Ore	Lime Content (% CaO)	Minimum Acid Requirements for Leaching (lbs. HCl/ton)	Minimum Acid Requirements for Leaching (lbs. H_2SO_4/ton)
Uravan	1.2	50	67
Wild Steer	1.0	90	121
Cactus Rat-Lot 411	2.2	110	148
Rico	3.0	80	107
Mineral Mountain-683	4.0	120	161
Mineral Mountain-750	5.7	160	215

Note: All tests were made with HCl in order to obtain direct comparison with the results from salt-roasted ores (see PART I, Table 33, page 92). Sulfuric acid consumptions were derived from a calculation of acid equivalents.

It may be observed, from the results, that the calcite concentration is perhaps the most important factor in determining the acid consumption by various ores, with other bases, such as Al_2O_3, playing minor but significant roles. Also, it must be concluded that the acid requirements for direct leaching of some of the ores are not exceedingly

large. It should be possible to extract uranium from Uravan ore, for instance, at a sulfuric acid cost of about one dollar per ton (sulfuric acid costs about 1-1/2 cents per pound, delivered at the mill). Further discussions of direct leach processes are given below (see "Discussion and Summary").

Impurities in Leach Solutions from Raw Ores

Considerable quantities of other minerals, besides those containing uranium and vanadium, are dissolved by an acid leach of raw ores. The amounts of the major impurities obtained by leaching 100 gm. samples of several raw ores are presented in Table 8. Nearly all of the calcium compounds in the ore are dissolved, even by very dilute acids, at room temperature. The amounts of soluble aluminum and iron (especially iron) are greatly increased with an increase in the acid strength or leaching temperature.

It may be remembered from Table 1 (PART I), that the Mineral Mountain ores are high in lime. Hence, from the results in Table 8, it may be concluded, in general, that the "high lime" ores will yield greater quantities of aluminum, as well as calcium, to the acid leach solutions.

In the right hand column of Table 8, the HCl equivalent to the impurities dissolved has been calculated (in lbs./ton of ore). These results serve well in demonstrating the increase in acid consumption by an ore with an increase in leaching concentration and/or temperature. Also, when taking into account the difference in leaching temperature, the

Table 8

Impurities Dissolved by Direct Leaching

Exp. No.	Type of Ore	HCl (%)	Temp. of Leach (°C.)	Extractions* by Acid Leach								HCL Consumed by Impurities (lbs.HCl per ton)
				Fe		Al		Mg		Ca		
				mg.	%	mg.	%	mg.	%	mg.	%	
I-478	Uravan	2	R.T.	50	8	11	1	37	7	795	99	32
I-479	Uravan	2	80	85	14	50	3	80	16	685	86	37
I-480	Uravan	5	R.T.	85	14	25	1	120	24	835	99	43
I-481	Uravan	5	80	310	50	75	4	130	25	825	99	56
H-208	Uravan	2.5	80	20	3	29	2	155	30	750	94	40
H-209	Uravan	5.0	80	220	35	31	2	220	43	755	94	52
H-318	Mineral Mountain-683	5	80	315	31	595	30	145	16	2280	80	153
H-319	Mineral Mountain-750	5	80	200	30	215	6	630	71	2670	66	161
H-320	Rico	5	80	130	10	140	11	60	6	1620	76	79
H-321	Rifle	5	80	160	14	140	12	425	33	1090	98	83

Leach Conditions: 100 g. ore (ground to -20 mesh) per 200 ml. of HCl solution agitated for 2 hours at 80°C. or room temperature (R.T.).

* Percentages calculated from head analysis (see Table 1).

Note: The amount of SiO_2 dissolved in the above leachings was less than 1%.

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results in Table 8 are in the expected agreement with room temperature consumption values in Table 7, which were derived by a different method (see preceding section).

Discussion and Summary

In the past, the Western mills have normally processed high vanadium ores, and since direct leaching treatments are not effective in recovering vanadium, such methods have not been seriously considered for mill practice. Large tonnages of the carnotite ores, however, contain only a small percentage of vanadium - so small, in fact, that the present vanadium recovery processes (PART I) cannot be applied at a profit. With these ores, a direct method to gain uranium would be preferable.

Indeed, at Monticello, Utah, a process for direct treatment of normal uranium-low vanadium ores with Na_2CO_3 solution is soon to be initiated. In this process, the raw ore is leached with hot 5% Na_2CO_3 solution and uranium is precipitated from the resultant liquors by the addition of H_2SO_4 to form "yellow-cake" (sodium uranyl vanadate). Since about one ton of leach solution will be expended in the plant for each ton of ore, the Na_2CO_3 cost for leaching will be about three dollars per ton of ore (taking Na_2CO_3, delivered, at 60 dollars per ton). Though this cost is fairly high, the carbonate process has several advantages in that (1) the precipitation process is simple and reasonably economical, and (2) the cost of a process is not materially changed when processing ores which bear large percentages of calcite.

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Uranium recoveries by acid leaching are better, perhaps than those from a carbonate process. The cost of the leaching step, will vary considerably according to the calcite concentration of the ore. Assuming a delivered cost for H_2SO_4 at 30 dollars per ton and taking the acid consumption values from Table 7, the leaching cost would be about 1 dollar per ore ton for Uravan ore (1/2% CaO), 2.40/ton for Mineral Mountain-683 (4.0% CaO), and 3.20/ton for Mineral Mountain-750 (5.7% CaO).

Certainly for a low-lime ore, the cost of acid leaching is very reasonable. The main difficulty with an "acid" process, however, lies in the recovery of uranium from the highly contaminated acid leach liquors. In certain existing mills (e.g., Rifle), using a salt-roasting, acid-leach process, the uranium is separated from the leach liquors by a complicated process in which the solution is taken past neutral several times by alternate additions of acids and bases (see Appendix B). As a consequence, the costs for labor and reagents are high. High enough, indeed, to make direct acid leaching compare unfavorably to a carbonate process.

With marked improvements in the process for recovering uranium from the acid liquors, it is more than probable that a direct acid leach process would be satisfactory for the treatment of low lime uranium ores in which the vanadium level is not high enough to justify recovery. Research directed toward methods for separating uranium from acid leach liquors is strongly suggested.

Other aspects of the Western ore developments also point up the value of such work. For instance, some ores contain uranium in a

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form (other than carnotite) which is soluble in acids but insoluble in carbonate solutions. These materials must, ultimately, be processed by an acid treatment.

Also it may be mentioned that fair tonnages of autunites are known to exist in the Western region. Since these deposits contain only small amounts of "impurity" minerals (such as minerals of Fe and Ca), it is probable that a fairly simple "acid method" could be worked out for their treatment.

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