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CONCENTRATION AND EXTRACTION OF VANADIUM FROM MINNESOTA VANADIFEROUS MAGNETITE

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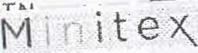
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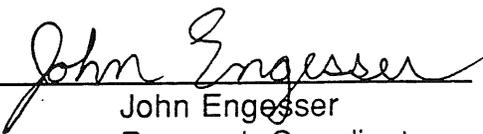

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CONSULTANTS' REPORT

**CONCENTRATION AND EXTRACTION
OF VANADIUM FROM MINNESOTA
VANADIFEROUS MAGNETITE**

Coleraine Minerals Research Laboratory

February 13, 1997

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ABSTRACT

A research project supported by the Minnesota Minerals Coordinating Committee was undertaken to determine the feasibility of extracting vanadium from Northeastern Minnesota vanadiferous-titaniferous magnetite ore. The ore sample that was used for this investigation was obtained for a research project that examined the feasibility of producing a synthetic rutile using a Minnesota ore. The titaniferous magnetite was crushed and the crusher product was fed to a rod mill. The rod mill product was discharged to a spiral classifier and the classifier discharge was run to a magnetic separator. The non-magnetic material was sent through an electrostatic separator. The electrostatic separator product was approximately 50 percent titanium dioxide or about 95 percent ilmenite (FeTiO_3). The vanadium that was present in the ore was concentrated into the magnetic material discharged from the magnetic separator. The magnetic portion of the ore is the material that was tested for vanadium concentration and extraction during this investigation. The project focused on the concentration and extraction of the vanadium by grinding, magnetic separation, flotation, salt roasting, leaching, precipitation, solvent extraction and ion exchange.

INTRODUCTION

Vanadium is an important metal in alloy production, in chemical production and in oil refining as a catalyst. Most of the vanadium that is used in the United States is imported from South Africa and South America. In the past, much of the U. S. produced vanadium came from uranium ores and vanadium production was dependent upon uranium demand. Presently most of the U.S. vanadium production is a by product of phosphate mining in the Western U.S. However, over 80% of the world vanadium supply is produced from vanadium containing titaniferous magnetite similar to that in the Duluth Gabbro Complex of northeastern Minnesota. The Duluth Gabbro Complex contains several oxide-rich ultramafic intrusions that contain significant quantities of titanium and vanadium. Previous work by U.S. Steel Exploration and Research has shown that there are deposits in the Duluth Complex that contain from 0.25 to 0.60 percent V_2O_5 and from 10 to 25 percent TiO_2 . The titanium occurs as ilmenite, FeTiO_3 , whereas, the vanadium mainly occurs as V^{+3} in the magnetite replacing the Fe^{+3} . The vanadium can therefore be separated from the ilmenite and gangue by magnetic separation. Ilmenite concentrates from these ores can contain 50 percent TiO_2 and magnetic concentrates can contain 1.6 percent V_2O_5 .

The ilmenite concentrate obtained from these ores can be used as a feed stock for the production of synthetic rutile. The market for high grade titanium dioxide concentrate (synthetic rutile) in the United States is about 400,000 tons per year, all of which is imported. A pilot plant operated by the Coleraine Minerals Research Laboratory in 1991, produced a high grade synthetic rutile (95% TiO_2) from a northeastern Minnesota ilmenite concentrate (50% TiO_2). During the production of the ilmenite concentrate, the titaniferous-magnetite ore was crushed and ground to minus 20 mesh and then

magnetically separated. The non-magnetic portion of the ore was further processed to obtain the ilmenite concentrate. The magnetic portion, which was 20 percent of the weight, contained 0.5 to 0.7 percent V_2O_5 . Further grinding and magnetic separation can provide a magnetic concentrate that contains 1 to 1.6 percent V_2O_5 . The magnetic concentrate can be used for a feed stock to produce high purity V_2O_5 , thus providing a second marketable product that can be produced from the Minnesota ore.

ACKNOWLEDGEMENTS

This study was funded by the Minnesota Minerals Coordinating Committee and the Minnesota Department of Natural Resources, whose support is gratefully acknowledged.

BACKGROUND

There are two basic techniques that are presently being used to recover vanadium from titaniferous magnetite. The first is a salt roast followed by leaching and subsequent solvent extraction, ion exchange and/or precipitation. The final product generally is 90 to 100 percent V_2O_5 . The second is a pyro-metallurgical technique in which the ore is reduced in a rotary kiln and then charged to an electric arc furnace followed by slaking ladles. The slag from the slaking ladles contains about 25 percent V_2O_5 .

The focus of this program was to determine the grade and recovery of vanadium oxide (V_2O_5) that can be obtained by salt roasting, leaching and extracting of Minnesota vanadiferous-titaniferous-magnetite ores. Pyro-metallurgical techniques for vanadium oxide concentration are beyond the scope of this program.

TEST PROGRAM

The primary objectives of the test program were to determine 1) The best physical separation techniques for vanadium concentration, 2) The sodium salt that maximizes the leachability of the vanadium from the concentrate after roasting, 3) The optimum roasting temperature, 4) The best separation techniques for removing the vanadium from the leachate, and 5) The grade and recovery of vanadium oxide.

The vanadiferous-titaniferous-magnetite ore that was used for the ilmenite research program for the production of synthetic rutile was ground to 20 mesh in a rod mill and magnetically separated using a drum-magnetic separator. The magnetic portion (vanadiferous-magnetite) from the drum separator was used as the feed material for this project.

Physical Separation.

Liberation Grinds. The vanadiferous-magnetite was subjected to standard wet liberation grinds of 6, 9, 12 and 17 minutes followed by a Davis Tube magnetic separation. The liberation mill products were analyzed for the percent of material that would pass through a 270-mesh screen. The Davis Tube magnetic concentrate was analyzed for iron, silica, and V_2O_5 . The weight of the Davis Tube feed and the weight of the magnetic product were reported so that the V_2O_5 recovery could be calculated. The Liberation Grind procedure is given in Appendix 1.

Ball Mill Grinds of Vanadiferous-Magnetite. Tests were run with a batch ball mill to determine the relationship in mill-discharge size vs grinding time. The sample was wet ground in a batch-ball mill to obtain 3 grinds. The time of the grinds were 22, 23.5 and 25 minutes which correlate to 88, 90 and 92 percent minus 270-mesh respectively. The ball-mill product for each grind was analyzed for the percent of material that would pass through a 270-mesh screen. Each ball-mill product was split to obtain samples for Davis Tube testing, batch-drum-magnetic separator testing, and salt roast testing. The magnetic concentrates from the Davis Tube tests and the magnetic-separator tests were analyzed for Fe, SiO_2 , and V_2O_5 . The Batch-Ball Grind procedure is given in Appendix 2. A complete screen analysis was performed on the ball-mill discharge of the 25 minute grind and also on the batch-drum-magnetic separator concentrate.

Amine Flotation. Four two kilogram samples of vanadiferous-magnetite were each subjected to a 25 minute batch-ball-mill grind followed by batch-magnetic separation. The magnetic concentrates were used in amine flotation testing. The flotation tests were run using Sherex MG 83 amine and methyl isobutyl carbinol as the frother. Four levels of amine were tested: 0.089, 0.156, 0.222, and 0.444 pounds of amine per long ton of magnetic concentrate. Timed froth samples were collected during each flotation test. The timed froth samples and the cell underflow were each analyzed for iron, silica and vanadium oxide. Rate equations were calculated for each flotation test. The flotation procedures are listed in Appendix 3. The vanadium oxide was concentrated in the cell underflow and the underflow products from each flotation test were then subjected to salt roasting and leaching tests.

Salt Roasting.

Initial Salt Roasting Tests. A sample of the vanadiferous-magnetite was pulverized to 100 percent passing 200 mesh and the pulverized material was magnetically separated with a Davis tube. Roasting tests were conducted with the magnetic portion of the Davis tube sample. Tests were conducted with sodium chloride, sodium carbonate and sodium sulfate at temperatures ranging from 800° C to 1000° C. These tests were carried out in platinum crucibles with 1 gram of sample and varying amounts salt. The roasts were leached with distilled water. The leachate was analyzed for vanadium, sodium and silica and the vanadium recoveries were calculated for each roast. From these tests, it was

determined that sodium carbonate would be used as the roasting salt for the remainder of the roasting tests. A description of each of the initial salt roasting tests is given in Appendix 4.

Sodium Carbonate Roasting Tests. Sodium carbonate roasting was performed on the "as is" batch ball mill discharge and the drum magnetic separator concentrate for each of the ball mill grinds (22.0, 23.5 and 25.0 minute grinds). Two sodium carbonate concentrations were tested - 9.1 and 16.6 percent. The roasts were performed at 900°C and 950°C. The product from each roast was leached in distilled water and the leachate was analyzed for vanadium, sodium and silica. Vanadium recoveries were calculated for each roast.

More extensive roasting and leaching tests were performed on the 25 minute ball mill grind product. In addition to the "as is" material and the drum magnetic separator concentrate, the following products from the 25 minute grind were roasted with sodium carbonate:

- 1) The Davis Tube magnetic concentrate.
- 2) Drum magnetic concentrate (5 passes through the separator).
- 3) Four amine flotation concentrate samples.

The sodium carbonate concentration for these roasting tests ranged from 9.1 percent to 23 percent. The roasting temperatures varied from 850°C to 1000°C. Each roasted product was leached in distilled water and the leachate was analyzed for vanadium, sodium and silica. Vanadium recoveries were calculated. A description of each of the sodium carbonate roasting tests is given in Appendix 4.

Green Ball Roasting. The flotation concentrate from the flotation tests that used 0.222 and 0.444 pounds of amine per long ton of concentrate were used for making green balls with 16 percent sodium carbonate. All of the green balls were dried at 105°C and then two balls of each type of concentrate were fired at each of the following temperatures respectively: 900°C, 950°C, 1000°C and 1050°C. The fired pellets were leached in distilled water. Each leachate was analyzed for vanadium, sodium and silica and the vanadium recovery was calculated.

Final Fired Pellet Product. Fourteen kilograms of sample were ground in a batch ball mill for 25 minutes and the ball mill discharge was then fed through a drum magnetic separator. The magnetic concentrate was recycled through the drum separator a total of 5 times. The magnetic concentrate was collected as the product. The final magnetic concentrate was subjected to batch flotation for 3 minutes using 0.222 pounds of amine per long ton of concentrate. The flotation under-flow was the final product and was then used to make green balls that contained 16 percent sodium carbonate. Approximately 5 kg of green balls were produced. The balls were dried at 105°C and then were fired at 1000°C. Three kilograms of the fired pellets were leached in 10 liters of distilled water

at 80°C for 8 hours. One kilogram of fired pellets was leached in 1 liter of distilled water at 80°C for 8 hours. These two leach liquors were analyzed for vanadium, sodium and silica. The leached pulp was analyzed for iron, silica, vanadium and sodium. Both the 1 liter and the 10 liter leach liquor samples were used in precipitation tests. The 10 liter sample was used in solvent extraction and ion exchange tests.

Extraction Tests

Precipitation. The 1 liter leach liquor sample was split into two 500 milliliter samples. One of the 500 ml samples was reduced to a volume of 200 milliliters by evaporation at 80°C; the second 500 ml sample was used "as is." A third 500 ml sample was split from the 10 liter leach liquor sample. These three leach liquors were used in vanadium precipitation tests. The three leach liquors samples were adjusted to a pH of 2.5 with sulfuric acid and heated to 80°C with agitation. The temperature of the samples was held at 80°C for 4 hours with continuous agitation. Each sample was then filtered and the filtered precipitates were dried, weighed and analyzed for vanadium, silica, sodium and iron. The precipitate samples were placed in platinum crucibles and heated to 1000°C for 2 hours. The resulting material was removed from the crucibles and analyzed for vanadium, silica, sodium and iron.

Ion Exchange. Four ion exchange resins were tested for vanadium capacity. Three of the resins were anion exchange resins - Dowex 1, Dowex 2, and Diaion WA30. The fourth resin was a cation exchange resin - Amberlite IR-130C.

Initial ion exchange tests were performed with the four resins by using a dilute neutral (pH 7) solution of vanadate ion.

A series of ion exchange tests were run using a 1 in 10 dilution of the leach liquor that was obtained by leaching 3 kilograms of fired pellets in 10 liters of water. These tests were run at four pH levels - 5.0, 7.0, 10.0, and 11.3 - with the three anion exchange resins. The cation exchange resin was not used in these tests.

Ion exchange tests were also run using the filtrate (liquid) from the precipitate tests with the three anion exchange resins. These tests were performed at the "as is" pH which was 2.5.

A complete description of each ion exchange test along with a description of each ion exchange resin is given in Appendix 5.

Solvent Extraction. The leach liquor used for the solvent extraction tests was obtain by leaching 3 kilograms of fired pellets in 10 liters of water. The solvent used to extract the vanadium from the aqueous-leach liquor was a quaternary amine called Aliquat 336. The extraction tests were performed at four pH levels - 4.5, 7.0, 10.0 and 12.5.

A vanadium solvent extraction test using the filtrate (liquid) from the precipitation tests and Aliquat 336 was also performed. This test was accomplished at the "as is" pH - 2.5.

A complete description of each solvent extraction test is given in Appendix 6.

PRESENTATION OF DATA

The vanadiferous-titaniferous-magnetite ore that was used to produce synthetic rutile was ground in a rod mill, discharged to a spiral classifier and magnetically separated in a drum-magnetic separator. The magnetic portion from the drum separator was used as the feed material for this project. The chemical analyses of the original ore head sample and the magnetic feed material for this project are given in Table 1.

Physical Separation.

Liberation Grinds. The chemical analyses of the Davis tube magnetic products for the "as is" sample and the 6, 9, 12, and 17 minute liberation grinds are listed in Table 2. The percent passing 270 mesh for the Davis tube feed is given in Table 2. The amount of vanadium oxide in the magnetic product ranged from 0.67 percent for the "as is" sample to 1.04 percent for the 17 minute grind, and the percent passing 270 mesh was 1.8 percent for the "as is" material and 87 percent for the 17 minute grind. The Davis-tube-vanadium recovery for the head sample is 89 percent and the recovery for the 17 minute grind is 53 percent. The silica is reduced from 7.8 percent in the head sample to 3.1 percent in the Davis tube product of the 17 minute grind. The liberation grind results are illustrated in Figures 1 through 3.

Batch Ball Mill Grinds. The percent passing 270 mesh for the 22 minute, 23.5 minute and 25 minute ball-mill grinds are 88, 91 and 94 percent respectively. The amount of vanadium oxide in the Davis tube magnetic product ranges from 1.03 percent for the 22 minute grind to 1.06 percent for the 25 minute grind. The vanadium recovery for the Davis tube product is 53 percent for all three grinds. The analyses of the Davis tube products are listed in Table 3 along with the amount of the ball mill discharge that passes through a 270 mesh screen. Figures 4 and 5 illustrate the relationship that exists between silica, vanadium oxide and grind time for the Davis tube product of both the liberation grinds and the batch ball mill grinds. Figures 6 and 7 represent the liberation of silica and vanadium oxide for the 22 minute, 23.5 minute and 25 minute ball-mill grinds.

Drum Magnetic Separation. The discharge from the 25 minute batch ball mill discharge was passed through a drum magnetic separator. The magnetic concentrate was recycled through the separator a total of 5 times. The vanadium oxide concentration in the magnetic product was increased from 0.89 percent after one pass to 0.96 percent after the fifth pass. Even after 5 passes through the separator, the vanadium oxide in the magnetic concentrate is approximately 0.1 percent lower than that of the Davis tube

concentrate. This is illustrated in Figure 8. A vanadium concentration of 0.96 percent in the final magnetic product represents a 67 percent recovery of vanadium and 47 percent weight recovery from the head sample. The analyses of the magnetic concentrates and the non-magnetic tails after the first and fifth passes are given in Table 4. Complete screen analyses of the magnetic-drum separator feed and the magnetic concentrate are given in Table 5. Figures 9, 10 and 11 represent the change in iron, silica and vanadium oxide by size fraction respectively from the feed to the magnetic concentrate.

Amine Flotation. The magnetic concentrate from the drum separator was subjected to four amine flotation tests. The concentration of vanadium oxide in the underflow ranged from 0.96 percent using 0.089 pounds of amine per long ton of concentrate to 1.19 percent using 0.444 pounds of amine per long ton of concentrate. This represents 98 percent to 53 percent vanadium recovery from the drum-separator concentrate respectively. The amount of vanadium that was recovered in the flotation underflow based on the vanadium in the ball mill discharge varied from 63 percent to 34 percent for 0.089 and 0.444 pounds of amine respectively. The vanadium oxide content of the Davis tube product for the 25 minute grind was 1.061 percent which represents 53 percent vanadium recovery. The flotation concentrate obtained using 0.222 pounds of amine had a vanadium oxide content of 1.057 percent which represents 52 percent vanadium recovery. This indicates that drum magnetic separation followed by amine flotation will result in a vanadium concentrate that is about the same grade as the Davis tube magnetic concentrate. The data for the four flotation tests are listed in Table 6. The flotation rate equations for silica removal and vanadium recovery are given in Table 7. Figures 12 and 13 illustrate the effect that amine flotation has on the concentration of vanadium oxide and silica with time, respectively. Figure 14 shows the relationship between amine usage and vanadium recovery.

Salt Roasting.

Initial Salt Roasting Tests. The initial salt roasting tests were conducted using the Davis Tube concentrate (1.06 percent V_2O_5) of a sample that was pulverized to 100 percent passing 200 mesh. Several 10 gram samples were run through the Davis Tube to ensure that enough sample was available for the salt roasting. The roasting tests were performed with sodium chloride, sodium sulfate and sodium carbonate at 800, 850, 900, 950, and 1000 degrees Celsius. Roasts were conducted using three concentrations of each salt. The sodium chloride concentrations were 9.1 percent, 23.1 percent and 37.5 percent. The vanadium recoveries for the sodium chloride roasts ranged from 45 percent with 9.1 percent salt at 800°C to 79 percent with 37.5 percent salt at 1000°C. The sodium sulfate concentrations that were tested were 9.1 percent, 16.7 percent and 23.1 percent. The vanadium recoveries for the sodium sulfate tests varied from 47 percent with 9.1 percent salt at 800°C to 89 percent with 23.1 percent salt at 1000°C. Sodium carbonate roasts were performed with 9.1 percent, 16.7 percent and 23.1 percent sodium carbonate. The vanadium recoveries using sodium carbonate as the salt ranged from 59 percent to 98 percent. The results of the initial roasting tests are listed in Table 8.

Figures 15, 16 and 17 illustrate the results of the sodium chloride, sodium sulfate and sodium carbonate roasting tests respectively. The remainder of the roasting test program was conducted with sodium carbonate as the roasting salt.

Sodium Carbonate Roasting Tests. Samples from the ball mill discharge were roasted with 9.1 percent and 16.7 percent sodium carbonate at 900 and 950 degrees Celsius. The vanadium recoveries were all less than 1 percent. The data for these tests are listed in Table 9.

The ball mill discharge for each grind (22 minute, 23.5 minute and 25 minute) was passed through the drum magnetic separator. The vanadium recovery from the separator was 75 percent, 73 percent and 68 percent for each grind respectively. A sample of the magnetic concentrate from magnetic separation of each grind was roasted with 9.1 percent and 16.7 percent sodium carbonate at 900 and 950 degrees Celsius. The vanadium recoveries for these roasts were between 1.3 percent and 34.7 percent of the vanadium from the magnetic concentrate. The total recovery of vanadium was 1 to 26 percent. The data are presented in Table 10.

The ball-mill discharge for the 25 minute grind was passed through the drum-magnetic separator and the magnetic concentrate was recycled through the separator 5 times. The vanadium recovery after 5 passes through the separator was 66.5 percent. The final magnetic concentrate was then roasted with 9.1 percent, 13 percent, 16.7 percent, and 20 percent sodium carbonate at 900°C and 950°C. The vanadium recoveries for these roasting tests ranged from 18 to 81 percent of the vanadium from the magnetic concentrate. The total vanadium recovery was 12 to 54 percent. The data for these tests are given in Table 11 and illustrated in Figure 18.

The ball mill discharge for the 25 minute grind was run through a Davis tube magnetic separator. The Davis tube weight recovery was 34.5 percent and the Davis tube vanadium recovery was 52 percent. The magnetic concentrate was roasted with 9.1 percent, 16.7 percent, 20 percent and 23.1 percent sodium carbonate at 850, 900, 950 and 1000 degrees Celsius. The vanadium recoveries for these tests ranged from 43 percent to 99 percent of the vanadium present in the Davis-tube magnetic concentrate. The total vanadium recoveries for the same roasting tests were between 22 and 52 percent based on the amount of vanadium in the ball mill discharge. These data are presented in Table 12 and illustrated in Figures 19 and 20.

The flotation concentrates obtained from the magnetic concentrate of the 25 minute ball mill grinds were roasted using 9.1 percent and 13 percent sodium carbonate at 900 and 950 degrees Celsius. The total vanadium recoveries including losses in flotation and magnetic separation were 7.6 to 22.0 percent when the flotation was performed with 0.089 pounds of amine per long ton of concentrate. Total vanadium recoveries for 0.156 pounds of amine ranged from 10.0 to 24.8 percent. Vanadium recoveries for 0.222

pounds of amine and 0.444 pounds of amine ranged from 18.7 to 23.6 percent and from 11.4 to 22.8 percent respectively. The data for these tests are given in Table 13.

Two additional roasting tests were performed with the flotation concentrate that was obtained using 0.444 pounds of amine per long ton. The roasts were performed with 16.7 percent sodium carbonate at 900 and 950 degrees Celsius. The total recoveries for these roasts were 30.4% and 30.8% respectively. The higher concentration of sodium carbonate increased the amount of leachable vanadium in the roasted material from 65 percent with 13 percent sodium carbonate to 85 percent with 16.7 percent sodium carbonate. These data are also listed in Table 13.

An excellent correlation exists between the silica concentration in the roasted sample and the vanadium recovery in the leach solutions. As the silica decreases, the vanadium recovery in the leach solution increases. A good correlation also exists between silica and vanadium recovery for the physical separations (ie. Davis Tube, magnetic separation and flotation). As the silica in the physically separated vanadium concentrate decreases, the vanadium recovery decreases. Data for these relationships are given in Table 14 and are plotted in Figures 21 and 22. Figure 21 demonstrates that vanadium recovery drops very rapidly as the amine usage increases during flotation. Examination of Figure 22 illustrates that the total vanadium recovery reaches a maximum when the silica concentration of the concentrate is approximately 4 percent.

Green Ball Roasting Tests. The flotation concentrate from the flotation test that used 0.222 pounds of amine per long ton of concentrate was used for making several green balls with 16 percent sodium carbonate. The green balls were dried and then two balls were fired at each of the following temperatures respectively: 900°C, 950°C, 1000°C and 1050°C. The fired pellets were leached in distilled water. The total vanadium recoveries were 40.1%, 41.8%, 43.8%, and 46.3% for each temperature respectively. The leach recoveries from the flotation concentrate were 78%, 81%, 85%, and 90% respectively. This data is given in Table 15. Figure 23 illustrates the vanadium recovery.

The flotation concentrate from the flotation test that used 0.444 pounds of amine per long ton of concentrate was used for making several green balls with 16 percent sodium carbonate. The green balls were dried and then two balls were fired at each of the following temperatures respectively: 900°C, 950°C, 1000°C and 1050°C. The fired pellets were leached in distilled water. The total vanadium recoveries were 32.2%, 32.7%, 33.1%, and 33.9% for each temperature respectively. The leach recoveries from the flotation concentrate were 93%, 94%, 95%, and 97% respectively. This data is given in Table 15. Figure 24 illustrates the vanadium recovery.

Final Fired Pellet Product. Fourteen kilograms of sample was ground in a ball mill for 25 minutes, then run through a drum-magnetic separator 5 times and finally floated with 0.222 pounds of amine per long ton of concentrate. The flotation under flow was used to make green balls with 16 percent sodium carbonate. Approximately 5 kg of

green balls were produced. The balls were dried at 105°C and then were fired at 1000°C. Three kilograms of the fired pellets were leached in 10 liters of distilled water at 80°C for 8 hours. The concentration of the 10 liter leach solution was 1402 milligrams of vanadium per liter. This represents a recovery of 86.9 percent of the vanadium from the pellets and a total vanadium recovery of 45 percent. One kilogram of fired pellets was leached in 1 liter of distilled water at 80°C for 8 hours. The concentration of the 1 liter leach solution was 3980 milligrams of Vanadium per liter. This represents a recovery of 74 percent of the vanadium from the pellets and a total vanadium recovery of 38 percent. The 1 liter leach liquor sample was used for the precipitation tests and the 10 liter sample was used for the precipitation tests, the solvent extraction tests and the ion exchange tests. The chemical analyses of the final pellet product along with the leach solutions are given in Table 16.

Extraction Tests

Precipitation. The 1 liter leach liquor sample (3980 mg V/l) was split into two 500 milliliter samples. One of the samples was reduced to a volume of 200 milliliters by evaporation at 80°C. The final Vanadium concentration of the evaporated sample was 9567 milligrams of vanadium per liter. Both leach liquors were adjusted to a pH of 2.5 with sulfuric acid and heated to 80°C with agitation. A 500 milliliter sample of the 10 liter (1402 mg V/l) leach solution was adjusted to pH 2.5 and heated to 80°C with agitation. The temperature of the samples were held at 80°C for 4 hours with continuous agitation. A vanadium "red cake" precipitate was formed. Each sample was then filtered and the filtered precipitates were dried, weighed and analyzed for vanadium, silica, sodium and iron. The vanadium recoveries from the leach solutions to the precipitates were 92.7 percent from the 1402 ppm V solution, 98.4 percent from the 3980 ppm V solution and 99.3 percent from the 9567 ppm V solution. These represent total vanadium recoveries of 41.5%, 37.5% and 37.8% respectively. The amount of vanadium oxide (V_2O_5) in the "red cake" precipitate is approximately 75 percent in each of the three precipitate samples. When the precipitates were roasted at 1000°C for 2 hours the amount of vanadium oxide in the roasted sample was approximately 90 percent. The results of the precipitate tests along with the "red cake" and roasted "red cake" analyses are given in Table 17.

Ion Exchange. The initial ion-exchange tests were run with three anion-exchange resins and one cation-exchange resin. These tests were performed with a pH 7 solution that contained 20.2 ppm Vanadium (39.2 ppm Vanadate(VO_3^-) ion). The results of the initial ion-exchange tests are given in Table 18. The calculated exchange capacities for the four resins are given in Table 19. As the concentration of the vanadate ion increases, the ion-exchange capacities of the anion exchange resins increase until a maximum is obtained. This is illustrated in Figure 25. The maximum vanadate capacities of the Amberlite IR-130C(cation resin), Dowex 1, Dowex 2, and Diaion WA30 were 0.0006, 0.124, 0.319, and 0.065 millimole per gram of resin respectively. These initial tests indicated that the Dowex 2 anion-exchange resin had the highest capacity for the

vanadate ion and that the Amberlite IR-130C had very limited capacity. No further tests were conducted with the Amberlite.

A series of ion-exchange tests were performed with a 1 in 10 dilution of the 1400 ppm leachate at pH 5, 7, 10, and 11.3 using each resin (Dowex 1, Dowex 2 and Diaion WA30). The initial pH of the leachate was 11.3. The results indicate that at all pH values the Dowex 2 resin performs better than the other 2 resins. Dowex 1 performs better than Diaion WA 30 at pH values greater than 7, however at pH values less than 7 the Diaion WA30 has a higher capacity than the Dowex 1. The Dowex 2 resin has a maximum exchange capacity at pH 10 and the Dowex 1 resin has a maximum exchange capacity at pH 11.3. The results of the pH tests are listed in Table 20 and illustrated in Figure 26.

Ion exchange tests were also run using the filtrate (liquid) from the precipitate tests with the three anion exchange resins. These tests were performed at pH 2.5 which is the pH of the precipitation reaction. The ion exchange capacities were 0.043, 0.071, and 0.047 millimole per gram for Dowex 1, Dowex 2 and Diaion WA 30 respectively. The results of these ion-exchange tests are given in Table 21.

Solvent Extraction. The leach liquor that was used in the extractions was 1400 ppm Vanadium with a pH of 12.5. The extraction tests were performed at pH levels of 4.5, 7.0, 11.3, and 12.5. The solvent used in the extractions was Aliquat 336. The highest extraction recoveries were obtained at pH 4.5. Three ratios of solvent to solute were tested at each pH. The ratios were 1:10, 1:5, and 2:5. The maximum amount of vanadium that was extracted from the vanadium solution with the solvent was 0.014 grams V per milliliter of solvent. The vanadium recoveries from the leach liquor ranged from 28 percent at pH 12.5 to 100 percent at pH 4.5. The solvent extraction results using the 1400 ppm vanadium leach liquor are found in Table 22 and illustrated in Figures 27 and 28.

Solvent extraction was also performed on the filtrate from the red-cake precipitation tests. The extraction was performed at the pH of the precipitation which is 2.5. The ratio of solvent to solute was 2:5 and the vanadium recovery from the filtrate was 98 percent. The results of the solvent extraction tests for the precipitate filtrate are given in Table 23.

CONCLUSIONS

Vanadium Oxide(98% V_2O_5) can be produced from Northeastern Minnesota vanadiferous-titaniferous magnetite ore by using standard mineral processing, leaching and extraction techniques.

The Vanadium recovery is 16 percent from the ore and 48 percent from the magnetic cobber concentrate.

Approximately 1.5 pounds of vanadium (2.7 pounds of V_2O_5) is recovered from each long ton of vanadiferous-titaniferous magnetite ore (rod-mill feed) processed. This is about 4.5 pounds of vanadium (7.9 pounds of V_2O_5) for each long ton of magnetic cobber concentrate.

The value of the vanadium recovered from each ton of crude ore at current prices (\$3.20 per pound of V_2O_5) would be \$8.64. The value of the vanadium that could be recovered by feeding the magnetic cobber concentrate would be \$25.28 per ton.

Vanadium recovery decreases as the silica concentration decreases during physical separation (grinding, magnetic separation and amine flotation).

Vanadium recovery during roasting and leaching increases with decreasing concentrations of silica in the roasted pellet.

Vanadium recovery increases with increasing concentrations of sodium carbonate in the roasted pellet until a 2 to 1 mole to mole ratio of N_2CO_3 to SiO_2 (approximately a 4 to 1 weight to weight ratio) is obtained. At this ratio almost 100 percent of the vanadium in the pellet is leached.

Vanadium recovery for this sample is maximized when the amount silica in the concentrate is about 4 percent and the concentration of sodium carbonate used for roasting is 16 percent. Additional research is necessary to determine how the vanadium recovery varies with changing ore characteristics and silica concentrations.

The final vanadium concentrate prior to pelletizing contains 58 percent iron, 4 percent silica, 13 percent titanium dioxide, 1 percent vanadium pentoxide, and 0.5 percent chromium oxide.

The leached vanadium pellets contain approximately 55 percent iron; however, they also have about 4 percent sodium and, therefore, would not be acceptable as iron units for blast furnace feed.

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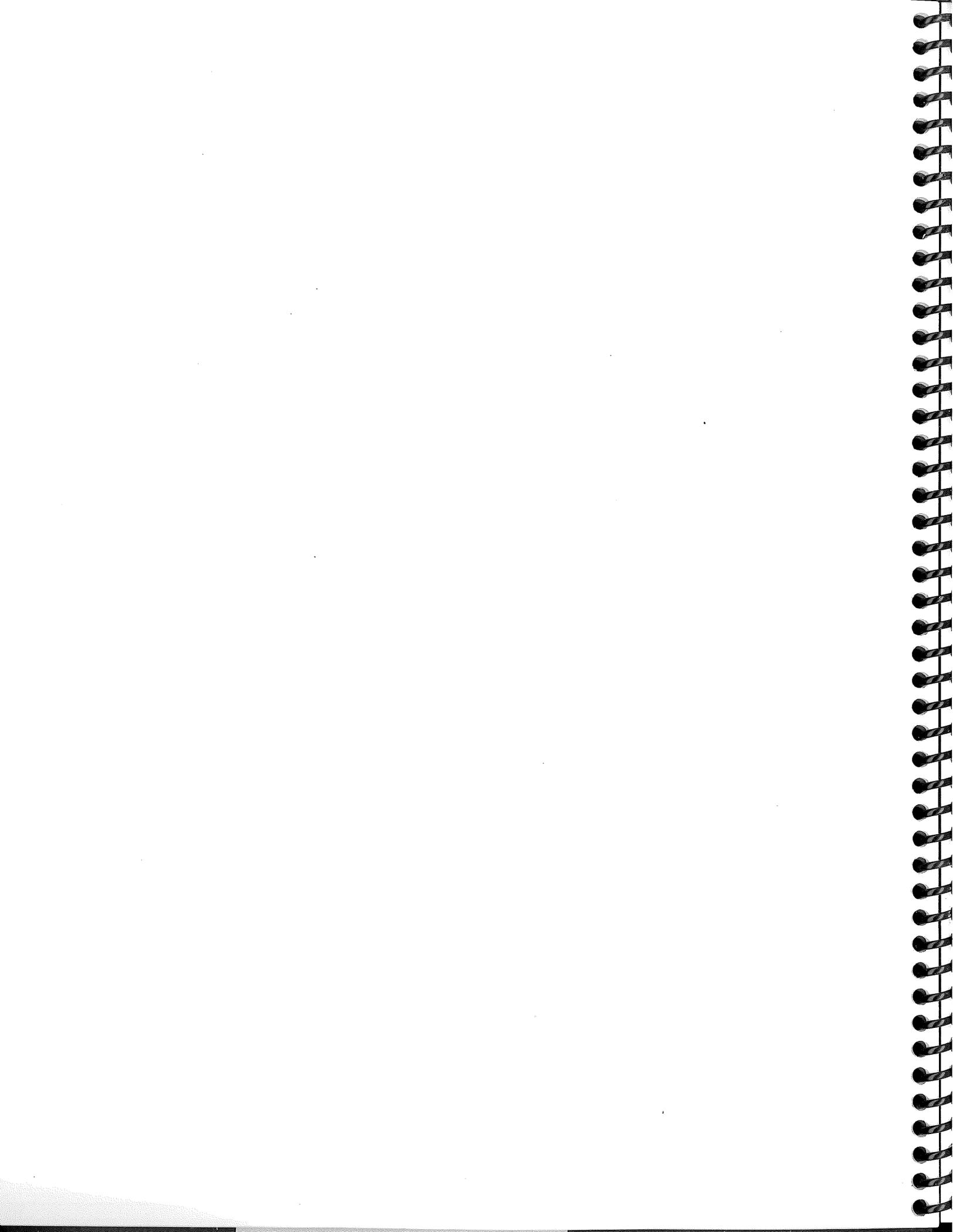


Table 1

Head Sample Chemical Analyses

| Sample Description | % Fe | % SiO ₂ | % TiO ₂ | % V ₂ O ₅ | % Cr | % Mn | % CaO | % MgO | % Al ₂ O ₃ | % Wt. V | % Rec. |
|---|---------|-----------------------|-----------------------|------------------------------------|---------|---------|----------|----------|-------------------------------------|------------|-----------|
| Longnose Titaniferous Magnetite | 26.3 | 25.10 | 19.20 | 0.428 | 0.089 | | 0.45 | 11.40 | 2.33 | | |
| Vanadium Project Head Sample (Magnetic Cobber Concentrate) | 42.1 | 7.76 | 25.83 | 0.678 | 0.188 | 0.29 | 0.25 | 7.21 | 0.98 | 20.1 | 32 |

Table 2

Davis Tube Liberation Grind Data

| Grind Time | %Fe | %SiO ₂ | %V ₂ O ₅ | %Cr | % Weight | %-270 | % V Recovery |
|------------|------|-------------------|--------------------------------|------|----------|-------|--------------|
| DT as is | 43.5 | 7.82 | 0.664 | 0.14 | 90.6 | 1.8 | 88.5 |
| 6 min | 50.1 | 5.46 | 0.757 | 0.27 | 55.7 | 32.7 | 62.0 |
| 9 min | 54.1 | 4.77 | 0.900 | 0.31 | 44.3 | 48.3 | 58.7 |
| 12 min | 57.5 | 3.89 | 0.932 | 0.35 | 39.9 | 62.7 | 54.7 |
| 17 min | 58.9 | 3.08 | 1.038 | 0.39 | 34.4 | 86.5 | 52.5 |

Table 3

Batch-Ball Mill Grind Data
Davis Tube Results

| Grind Time (minute) | %SiO ₂ | %V ₂ O ₅ | %Weight | %-270 | % V Recovery |
|---------------------------|-------------------|--------------------------------|---------|-------|-----------------|
| 22.0 | 3.07 | 1.033 | 34.35 | 87.8 | 52.2 |
| 23.5 | 2.94 | 1.052 | 33.94 | 91.0 | 52.5 |
| 25.0 | 2.87 | 1.061 | 33.48 | 94.0 | 52.2 |

Table 4

Drum Magnetic Separator Data

One Pass Through The Magnetic Separator

| Time (min) | Type | %Fe | %SiO ₂ | %TiO ₂ | %V ₂ O ₅ | Weight (grams) | %V Rec |
|---------------|-------|------|-------------------|-------------------|--------------------------------|-------------------|--------|
| 25.0 | Conc. | 54.6 | 4.92 | 14.11 | 0.905 | 1021 | 68.8 |
| 25.0 | Tail | 29.1 | 10.69 | 38.09 | 0.411 | 979 | |
| 23.5 | Conc. | 52.8 | 4.88 | 15.33 | 0.869 | 1142 | 72.8 |
| 23.5 | Tail | 27.8 | 11.35 | 39.33 | 0.438 | 858 | |
| 22.0 | Conc. | 51.9 | 5.11 | 16.25 | 0.836 | 1228 | 74.9 |
| 22.0 | Tail | 26.5 | 11.86 | 39.89 | 0.458 | 772 | |

Five Pass Through The Magnetic Separator

| | | | | | | | |
|------|-------|------|-------|-------|-------|------|------|
| 25.0 | Conc. | 55.8 | 4.04 | 13.02 | 0.960 | 6605 | 66.5 |
| 25.0 | Tail | 29.9 | 11.09 | 37.27 | 0.435 | 7395 | |

Table 5

Screen Analyses of 25 Minute Ball Mill Grind

Screen Analysis - Vanadium 25 Minute Grind - Mag Sep Feed

| Screen | Mass, g | %Wt | %Fe | %SiO ₂ | %V ₂ O ₅ | %V ₂ O ₅ by Size | %SiO ₂ by Size |
|------------|---------|--------|------|-------------------|--------------------------------|---|------------------------------|
| +20 | 0.0 | 0.00 | 48.5 | 9.85 | 0.559 | 0.00 | 0.00 |
| -20/+65 | 0.2 | 0.10 | 48.5 | 9.85 | 0.559 | 0.00 | 0.01 |
| -65/+100 | 0.1 | 0.05 | 48.5 | 9.85 | 0.559 | 0.00 | 0.00 |
| -100/+200 | 1.7 | 0.86 | 42.5 | 7.43 | 0.724 | 0.01 | 0.06 |
| -200/+270 | 10.1 | 5.09 | 44.1 | 6.98 | 0.747 | 0.04 | 0.35 |
| -270/+400 | 16.8 | 8.46 | 44.2 | 6.99 | 0.740 | 0.06 | 0.59 |
| -400/+500 | 44.3 | 22.31 | 44.2 | 6.71 | 0.735 | 0.16 | 1.50 |
| -500 | 125.4 | 63.14 | 42.3 | 8.29 | 0.670 | 0.42 | 5.23 |
| Feed Calc. | 198.6 | 100.00 | 43.0 | 7.76 | 0.695 | | |
| Feed Assay | | | 42.1 | 7.76 | 0.678 | | |

Screen Analysis - Vanadium 25 Minute Grind - 5 Separator Passes

| Screen | Mass, g | %Wt | %Fe | %SiO ₂ | %V ₂ O ₅ | %V ₂ O ₅ by Size | %SiO ₂ by Size |
|-------------|---------|--------|------|-------------------|--------------------------------|---|------------------------------|
| +20 | 0.0 | 0.00 | 49.8 | 6.72 | 0.870 | 0.00 | 0.00 |
| -20/+65 | 0.0 | 0.00 | 49.8 | 6.72 | 0.870 | 0.00 | 0.00 |
| -65/+100 | 0.0 | 0.00 | 49.8 | 6.72 | 0.870 | 0.00 | 0.00 |
| -100/+200 | 2.1 | 0.99 | 49.8 | 6.72 | 0.870 | 0.01 | 0.07 |
| -200/+270 | 13.2 | 6.20 | 50.3 | 5.84 | 0.930 | 0.06 | 0.36 |
| -270/+400 | 23.9 | 11.22 | 51.6 | 5.23 | 0.927 | 0.10 | 0.59 |
| -400/+500 | 48.2 | 22.63 | 51.0 | 4.57 | 0.980 | 0.22 | 1.03 |
| -500 | 125.6 | 58.97 | 55.1 | 3.50 | 0.955 | 0.56 | 2.06 |
| Conc. Calc. | 213.0 | 100.00 | 53.4 | 4.11 | 0.955 | | |
| Conc. Assay | | | 55.7 | 4.09 | 0.972 | | |

Table 6

Flotation Data

Flotation Test 1 0.089 pounds Amine per Long Ton Concentrate

| Sample | %V2O5 Assay | %SiO2 Assay | Calc %SiO2 | Time (min) | Mass (g) | V2O5 %Recovery |
|-----------|----------------|----------------|---------------|---------------|-------------|-------------------|
| Head | | | 4.09 | 0.0 | | 100.0 |
| Froth | 0.476 | 11.37 | 4.01 | 0.5 | 11.0 | 99.4 |
| Froth | 0.446 | 11.44 | 3.94 | 1.0 | 8.5 | 99.0 |
| Froth | 0.424 | 11.44 | 3.91 | 1.5 | 4.0 | 98.9 |
| Froth | 0.442 | 10.77 | 3.89 | 2.0 | 3.5 | 98.7 |
| Froth | 0.502 | 8.98 | 3.80 | 3.0 | 16.8 | 97.8 |
| Underflow | 0.961 | 3.80 | | | 959.2 | |

Flotation Test 2 0.156 pounds Amine per Long Ton Concentrate

| Sample | %V2O5 Assay | %SiO2 Assay | Calc %SiO2 | Time (min) | Mass (g) | V2O5 %Recovery |
|-----------|----------------|----------------|---------------|---------------|-------------|-------------------|
| Head | | | 4.08 | 0.0 | | 100.0 |
| Froth | 0.655 | 6.48 | 3.90 | 0.5 | 69.7 | 95.2 |
| Froth | 0.658 | 6.08 | 3.79 | 1.0 | 45.0 | 92.2 |
| Froth | 0.643 | 5.72 | 3.71 | 1.5 | 35.2 | 89.8 |
| Froth | 0.661 | 5.45 | 3.65 | 2.0 | 29.3 | 87.8 |
| Froth | 0.673 | 5.18 | 3.55 | 3.0 | 48.9 | 84.4 |
| Underflow | 1.044 | 3.55 | | | 776.2 | |

Flotation Test 3 0.222 pounds Amine per Long Ton Concentrate

| Sample | %V2O5 Assay | %SiO2 Assay | Calc %SiO2 | Time (min) | Mass (g) | V2O5 %Recovery |
|-----------|----------------|----------------|---------------|---------------|-------------|-------------------|
| Head | | | 4.09 | 0.0 | | 100.0 |
| Froth | 0.689 | 5.91 | 3.93 | 0.5 | 84.3 | 93.9 |
| Froth | 0.700 | 5.39 | 3.81 | 1.0 | 68.5 | 88.9 |
| Froth | 0.704 | 5.12 | 3.73 | 1.5 | 49.2 | 85.2 |
| Froth | 0.689 | 4.94 | 3.67 | 2.0 | 35.0 | 82.7 |
| Froth | 0.742 | 4.84 | 3.56 | 3.0 | 67.1 | 77.5 |
| Underflow | 1.057 | 3.56 | | | 697.4 | |

Flotation Test 4 0.444 pounds Amine per Long Ton Concentrate

| Sample | %V2O5 Assay | %SiO2 Assay | Calc %SiO2 | Time (min) | Mass (g) | V2O5 %Recovery |
|-----------|----------------|----------------|---------------|---------------|-------------|-------------------|
| Head | | | 4.03 | 0.0 | | 100.0 |
| Froth | 0.718 | 4.75 | 3.88 | 0.5 | 169.6 | 87.4 |
| Froth | 0.788 | 4.52 | 3.77 | 1.0 | 126.2 | 77.1 |
| Froth | 0.827 | 4.40 | 3.67 | 1.5 | 91.8 | 69.3 |
| Froth | 0.882 | 4.22 | 3.60 | 2.0 | 67.7 | 63.1 |
| Froth | 0.896 | 4.05 | 3.48 | 3.0 | 117.4 | 52.3 |
| Underflow | 1.186 | 3.48 | | | 426.5 | |

Table 7

Equations for Amine Flotation of Magnetic Concentrate

Silica Equations for Amine Flotation

| Test Description | m | b | k | R ² |
|-----------------------------|-------|-------|-------|----------------|
| Flotation 0.089 lb Amine/LT | 0.416 | 3.666 | 0.357 | 0.9858 |
| Flotation 0.156 lb Amine/LT | 0.612 | 3.460 | 0.616 | 0.9983 |
| Flotation 0.222 lb Amine/LT | 0.645 | 3.444 | 0.551 | 0.9979 |
| Flotation 0.444 lb Amine/LT | 0.766 | 3.261 | 0.413 | 0.9996 |

Vanadium Oxide (V₂O₅) Equations for Amine Flotation

| Test Description | m | b | k | R ² |
|-----------------------------|--------|-------|-------|----------------|
| Flotation 0.089 lb Amine/LT | -0.073 | 1.014 | 0.107 | 0.9829 |
| Flotation 0.156 lb Amine/LT | -0.151 | 1.108 | 0.288 | 0.9994 |
| Flotation 0.222 lb Amine/LT | -0.189 | 1.139 | 0.276 | 0.9998 |
| Flotation 0.444 lb Amine/LT | -0.425 | 1.396 | 0.232 | 0.9983 |

Table 8

Initial Salt Roast Data of Davis Tube Concentrate

| Temp, °C | Tests 1-15 | Tests 16-30 | Tests 31-45 | Tests 1-15 | Tests 16-30 | Tests 31-45 |
|----------|---------------|--|--|---------------|----------------------------------|----------------------------------|
| | V Rec NaCl | V Rec Na ₂ SO ₄ | V Rec Na ₂ CO ₃ | %NaCl | %Na ₂ SO ₄ | %Na ₂ CO ₃ |
| 800 | 44.5 | 47.2 | 58.6 | 9.1 | 9.1 | 9.1 |
| 800 | 48.6 | 49.1 | 66.8 | 23.1 | 16.7 | 16.7 |
| 800 | 53.5 | 51.2 | 71.4 | 37.5 | 23.1 | 23.1 |
| 850 | 52.1 | 49.1 | 60.2 | 9.1 | 9.1 | 9.1 |
| 850 | 55.8 | 50.2 | 80.5 | 23.1 | 16.7 | 16.7 |
| 850 | 57.2 | 52.3 | 82.9 | 37.5 | 23.1 | 23.1 |
| 900 | 54.6 | 60.2 | 64.8 | 9.1 | 9.1 | 9.1 |
| 900 | 56.8 | 63.6 | 92.2 | 23.1 | 16.7 | 16.7 |
| 900 | 58.9 | 64.9 | 97.1 | 37.5 | 23.1 | 23.1 |
| 950 | 61.5 | 62.1 | 51.1 | 9.1 | 9.1 | 9.1 |
| 950 | 66.4 | 71.2 | 92.1 | 23.1 | 16.7 | 16.7 |
| 950 | 68.2 | 77.6 | 98.0 | 37.5 | 23.1 | 23.1 |
| 1000 | 71.2 | 61.5 | 48.6 | 9.1 | 9.1 | 9.1 |
| 1000 | 74.6 | 81.2 | 91.5 | 23.1 | 16.7 | 16.7 |
| 1000 | 79.2 | 88.5 | 98.1 | 37.5 | 23.1 | 23.1 |

Table 9

Ball Mill Grind Roast Tests
Sodium Carbonate as the Salt

| Test No. | Grind Time (min) | Sample Description | Roast Temp, C | Na ₂ CO ₃ mass | % V Recovery | ppm V |
|----------|------------------|--------------------|---------------|--------------------------------------|--------------|-------|
| 46 | 22.0 | Ball Mill Dis. | 900 | 9.2 | 0.10 | 0.020 |
| 47 | 22.0 | Ball Mill Dis. | 950 | 9.2 | 0.16 | 0.030 |
| 48 | 23.5 | Ball Mill Dis. | 900 | 9.2 | 0.10 | 0.020 |
| 49 | 23.5 | Ball Mill Dis. | 950 | 9.2 | 0.11 | 0.020 |
| 50 | 25.0 | Ball Mill Dis. | 900 | 9.1 | 0.10 | 0.020 |
| 51 | 25.0 | Ball Mill Dis. | 950 | 9.2 | 0.29 | 0.056 |
| 52 | 22.0 | Ball Mill Dis. | 900 | 16.7 | 0.26 | 0.050 |
| 53 | 22.0 | Ball Mill Dis. | 950 | 16.7 | 0.62 | 0.119 |
| 54 | 23.5 | Ball Mill Dis. | 900 | 16.7 | 0.38 | 0.072 |
| 55 | 23.5 | Ball Mill Dis. | 950 | 16.7 | 0.56 | 0.106 |
| 56 | 25.0 | Ball Mill Dis. | 900 | 16.7 | 0.25 | 0.047 |
| 57 | 25.0 | Ball Mill Dis. | 950 | 16.7 | 0.39 | 0.075 |

Table 10

Magnetic Separator Concentrate Roast Tests
Salt Roasts with Sodium Carbonate

| Test No. | Grind Time (min) | Sample Description | Roast Temp, C | %NaCO ₃ | Leach % V ₂ O ₅ Recovery | Total % V ₂ O ₅ Recovery | ppm V | ppm Na | ppm Si | Sample mass, g | Theor. ppm | Na ₂ CO ₃ mass, g |
|----------|------------------|--------------------|---------------|--------------------|--|--|-------|--------|--------|----------------|------------|---|
| 58 | 22.0 | Magnetic Conc. | 900 | 9.2 | 2.5 | 1.9 | 0.59 | 5.25 | 0.55 | 1.0011 | 23.6 | 0.1012 |
| 59 | 22.0 | Magnetic Conc. | 950 | 9.1 | 1.4 | 1.1 | 0.34 | 4.61 | 0.75 | 1.0001 | 23.5 | 0.1001 |
| 60 | 23.5 | Magnetic Conc. | 900 | 9.1 | 3.0 | 2.2 | 0.73 | 5.62 | 0.10 | 1.0008 | 24.4 | 0.1006 |
| 61 | 23.5 | Magnetic Conc. | 950 | 9.2 | 1.3 | 0.9 | 0.31 | 4.30 | 0.94 | 1.0007 | 24.4 | 0.1011 |
| 62 | 25.0 | Magnetic Conc. | 900 | 9.1 | 2.4 | 1.6 | 0.60 | 5.05 | 0.44 | 1.0007 | 25.1 | 0.0999 |
| 63 | 25.0 | Magnetic Conc. | 950 | 9.1 | 1.6 | 1.1 | 0.40 | 5.69 | 1.10 | 1.0005 | 25.1 | 0.1005 |
| 64 | 22.0 | Magnetic Conc. | 900 | 16.7 | 31.4 | 23.5 | 7.38 | 27.06 | 1.53 | 1.0001 | 23.5 | 0.2008 |
| 65 | 22.0 | Magnetic Conc. | 950 | 16.6 | 15.9 | 11.9 | 3.75 | 17.37 | 0.56 | 1.0003 | 23.5 | 0.1996 |
| 66 | 23.5 | Magnetic Conc. | 900 | 16.6 | 34.7 | 25.3 | 8.45 | 28.11 | 0.64 | 1.0005 | 24.4 | 0.1996 |
| 67 | 23.5 | Magnetic Conc. | 950 | 16.7 | 33.8 | 24.6 | 8.22 | 29.80 | 1.74 | 0.9989 | 24.3 | 0.2004 |
| 68 | 25.0 | Magnetic Conc. | 900 | 16.7 | 34.2 | 23.6 | 8.59 | 25.96 | 0.79 | 0.9990 | 25.1 | 0.2000 |
| 69 | 25.0 | Magnetic Conc. | 950 | 16.7 | 34.7 | 23.8 | 8.71 | 30.85 | 1.43 | 1.0007 | 25.1 | 0.2001 |

Table 11

Salt Roasting Data of Drum Magnetic Separator Concentrate
Sodium Carbonate as the Roasting Salt

| Test No. | Grind Time (min) | Sample Description | Roast Temp, C | %Na ₂ CO ₃ | Leach % V ₂ O ₅ Recovery | Total % V ₂ O ₅ Recovery | ppm V | ppm Na | ppm Si | Sample mass, g | Theor. ppm | Na ₂ CO ₃ mass, g |
|----------|------------------|------------------------|---------------|----------------------------------|--|--|-------|--------|--------|----------------|------------|---|
| 70 | 25.0 | 5 Magnetic Separations | 900 | 9.1 | 18.0 | 11.9 | 5.30 | 18.09 | 11.89 | 1.0003 | 29.5 | 0.1000 |
| 71 | 25.0 | 5 Magnetic Separations | 950 | 9.0 | 14.0 | 9.3 | 4.13 | 13.71 | 1.19 | 1.0007 | 29.5 | 0.0995 |
| 72 | 25.0 | 5 Magnetic Separations | 900 | 13.1 | 50.8 | 33.8 | 14.98 | 38.93 | 0.81 | 0.9995 | 29.5 | 0.1511 |
| 73 | 25.0 | 5 Magnetic Separations | 950 | 13.1 | 40.3 | 26.8 | 11.90 | 38.72 | 1.40 | 1.0010 | 29.5 | 0.1510 |
| 74 | 25.0 | 5 Magnetic Separations | 900 | 16.7 | 78.4 | 52.1 | 23.17 | 67.91 | 1.76 | 1.0012 | 29.6 | 0.2009 |
| 75 | 25.0 | 5 Magnetic Separations | 950 | 16.7 | 69.8 | 46.4 | 20.60 | 62.06 | 1.85 | 1.0001 | 29.5 | 0.2008 |
| 76 | 25.0 | 5 Magnetic Separations | 900 | 20.0 | 89.3 | 59.4 | 26.41 | 86.94 | 2.35 | 1.0015 | 29.6 | 0.2508 |
| 77 | 25.0 | 5 Magnetic Separations | 950 | 20.0 | 81.0 | 53.9 | 23.92 | 78.28 | 2.09 | 1.0003 | 29.5 | 0.2498 |

Table 12

Salt Roasting of 25 minute Ball Mill Grind Davis Tube Concentrates

| Test No. | Grind Time (min) | Sample Description | Roast Temp, C | %Na ₂ CO ₃ | Leach % V ₂ O ₅ Recovery | Total % V ₂ O ₅ Recovery | ppm V | ppm Na | ppm Si | Sample mass, g | Theor. ppm | Na ₂ CO ₃ mass, g |
|----------|------------------|--------------------|---------------|----------------------------------|--|--|-------|--------|--------|----------------|------------|---|
| 78 | 25.0 | Davis Tube Conc. | 850 | 9.1 | 61.5 | 32.1 | 19.45 | 53.46 | 5.91 | 1.0001 | 31.7 | 0.1001 |
| 79 | 25.0 | Davis Tube Conc. | 850 | 16.7 | 75.0 | 39.2 | 23.74 | 137.99 | 6.23 | 0.9999 | 31.6 | 0.2003 |
| 80 | 25.0 | Davis Tube Conc. | 850 | 20.0 | 80.3 | 41.9 | 25.40 | 155.72 | 5.76 | 0.9995 | 31.6 | 0.2506 |
| 81 | 25.0 | Davis Tube Conc. | 850 | 23.1 | 83.4 | 43.6 | 26.41 | 200.32 | 6.32 | 1.0001 | 31.7 | 0.3007 |
| 82 | 25.0 | Davis Tube Conc. | 900 | 9.1 | 65.7 | 34.3 | 20.79 | 55.52 | 4.50 | 1.0000 | 31.6 | 0.1001 |
| 83 | 25.0 | Davis Tube Conc. | 900 | 16.7 | 89.5 | 46.7 | 28.36 | 144.88 | 5.55 | 1.0008 | 31.7 | 0.2007 |
| 84 | 25.0 | Davis Tube Conc. | 900 | 20.1 | 91.6 | 47.8 | 28.98 | 168.60 | 4.74 | 0.9999 | 31.6 | 0.2508 |
| 85 | 25.0 | Davis Tube Conc. | 900 | 23.1 | 98.7 | 51.5 | 31.22 | 208.12 | 3.99 | 0.9997 | 31.6 | 0.3003 |
| 86 | 25.0 | Davis Tube Conc. | 950 | 9.1 | 43.4 | 22.7 | 13.75 | 39.76 | 1.78 | 1.0007 | 31.7 | 0.1001 |
| 87 | 25.0 | Davis Tube Conc. | 950 | 16.7 | 87.7 | 45.8 | 27.73 | 91.05 | 2.42 | 0.9995 | 31.6 | 0.2000 |
| 88 | 25.0 | Davis Tube Conc. | 950 | 20.0 | 91.6 | 47.8 | 28.98 | 139.40 | 3.13 | 0.9997 | 31.6 | 0.2500 |
| 89 | 25.0 | Davis Tube Conc. | 950 | 23.1 | 97.7 | 51.0 | 30.93 | 176.69 | 3.74 | 1.0005 | 31.7 | 0.3003 |
| 90 | 25.0 | Davis Tube Conc. | 1000 | 9.2 | 45.5 | 23.8 | 14.41 | 37.03 | 1.31 | 0.9998 | 31.6 | 0.1011 |
| 91 | 25.0 | Davis Tube Conc. | 1000 | 16.7 | 90.0 | 47.0 | 28.48 | 72.79 | 1.76 | 1.0001 | 31.7 | 0.2004 |
| 92 | 25.0 | Davis Tube Conc. | 1000 | 20.0 | 94.9 | 49.5 | 30.08 | 83.01 | 1.94 | 1.0018 | 31.7 | 0.2501 |
| 93 | 25.0 | Davis Tube Conc. | 1000 | 23.1 | 98.0 | 51.2 | 31.01 | 94.84 | 1.74 | 0.9998 | 31.6 | 0.2995 |

Table 13

Salt Roasting of Flotation Concentrates
Sodium Carbonate as the Salt

| Test No. | Grind Time (min) | Sample Description | Roast Temp, C | %Na ₂ CO ₃ | %V Leach Recovery | %Total V Rec. | ppm V | ppm Na | ppm Si | Sample mass, g | Theor. ppm | Na ₂ CO ₃ mass |
|----------|------------------|------------------------|---------------|----------------------------------|-------------------|---------------|-------|--------|--------|----------------|------------|--------------------------------------|
| 94 | 25.0 | Flot Conc. 0.089 lb/LT | 900 | 9.1 | 17.1 | 11.2 | 4.61 | 15.48 | 1.49 | 1.0001 | 26.9 | 0.0996 |
| 95 | 25.0 | Flot Conc. 0.089 lb/LT | 900 | 13.0 | 33.6 | 21.9 | 9.04 | 31.98 | 1.34 | 1.0005 | 26.9 | 0.1492 |
| 96 | 25.0 | Flot Conc. 0.089 lb/LT | 950 | 9.1 | 11.6 | 7.6 | 3.13 | 12.20 | 4.17 | 0.9999 | 26.9 | 0.0998 |
| 97 | 25.0 | Flot Conc. 0.089 lb/LT | 950 | 13.0 | 33.1 | 21.6 | 8.91 | 27.46 | 1.19 | 1.0001 | 26.9 | 0.1496 |
| 98 | 25.0 | Flot Conc. 0.156 lb/LT | 900 | 9.1 | 17.7 | 10.0 | 5.18 | 15.32 | 0.81 | 0.9996 | 29.2 | 0.0995 |
| 99 | 25.0 | Flot Conc. 0.156 lb/LT | 900 | 13.1 | 43.9 | 24.7 | 12.84 | 36.90 | 1.23 | 1.0006 | 29.3 | 0.1506 |
| 100 | 25.0 | Flot Conc. 0.156 lb/LT | 950 | 9.1 | 25.2 | 14.2 | 7.37 | 22.07 | 1.26 | 1.0002 | 29.2 | 0.1004 |
| 101 | 25.0 | Flot Conc. 0.156 lb/LT | 950 | 13.0 | 44.0 | 24.8 | 12.86 | 32.90 | 3.62 | 1.0005 | 29.3 | 0.1499 |
| 102 | 25.0 | Flot Conc. 0.222 lb/LT | 900 | 9.0 | 36.1 | 18.7 | 10.69 | 31.75 | 1.46 | 1.0007 | 29.6 | 0.0993 |
| 103 | 25.0 | Flot Conc. 0.222 lb/LT | 900 | 13.1 | 45.5 | 23.6 | 13.49 | 45.18 | 1.72 | 1.0007 | 29.6 | 0.1503 |
| 104 | 25.0 | Flot Conc. 0.222 lb/LT | 950 | 9.1 | 23.2 | 12.0 | 6.86 | 19.63 | 1.37 | 1.0004 | 29.6 | 0.1007 |
| 105 | 25.0 | Flot Conc. 0.222 lb/LT | 950 | 13.1 | 42.2 | 21.9 | 12.50 | 36.56 | 1.28 | 1.0004 | 29.6 | 0.1508 |
| 106 | 25.0 | Flot Conc. 0.444 lb/LT | 900 | 9.2 | 34.9 | 12.2 | 11.58 | 30.40 | 1.48 | 1.0000 | 33.2 | 0.1008 |
| 107 | 25.0 | Flot Conc. 0.444 lb/LT | 900 | 13.1 | 64.1 | 22.4 | 21.29 | 52.06 | 1.68 | 0.9998 | 33.2 | 0.1504 |
| 108 | 25.0 | Flot Conc. 0.444 lb/LT | 900 | 16.7 | 86.9 | 30.4 | 28.88 | 84.04 | 3.99 | 1.0004 | 33.2 | 0.1999 |
| 109 | 25.0 | Flot Conc. 0.444 lb/LT | 950 | 9.1 | 32.5 | 11.4 | 10.79 | 27.49 | 1.40 | 0.9997 | 33.2 | 0.1000 |
| 110 | 25.0 | Flot Conc. 0.444 lb/LT | 950 | 13.1 | 65.4 | 22.8 | 21.74 | 52.09 | 1.49 | 1.0006 | 33.2 | 0.1502 |
| 111 | 25.0 | Flot Conc. 0.444 lb/LT | 950 | 16.7 | 88.1 | 30.8 | 29.27 | 74.25 | 2.22 | 1.0000 | 33.2 | 0.2003 |

Table 14

Vanadium Recovery Data
Davis Tube, Magnetic Separator, Flotation, and Roast-Leach

Davis Tube Concentrates

| Sample Description | %SiO ₂ | Physical % V Rec. | Leach % V Rec. | Total % V Rec. |
|---------------------|-------------------|-------------------|----------------|----------------|
| As is" Head Sample | 7.82 | 88.5 | | |
| 6 min Lib Grind | 5.46 | 62.0 | | |
| 9 min Lib Grind | 4.77 | 58.7 | | |
| 12 min Lib Grind | 3.89 | 54.7 | | |
| 17 min Lib Grind | 3.08 | 52.5 | | |
| 22 min Ball Grind | 3.07 | 52.2 | | |
| 23.5 min Ball Grind | 2.94 | 52.5 | | |
| 25 min Ball Grind | 2.87 | 52.2 | 88.6 | 46.2 |

Magnetic Separator and Flotation Samples

| | | | | |
|---------------------------|------|-------|------|------|
| Head Sample | 7.76 | 100.0 | 0.2 | 0.2 |
| 1 Mag Sep. 22 Min Grind | 5.11 | 74.9 | 23.7 | 17.7 |
| 1 Mag Sep. 25 Min Grind | 4.92 | 68.8 | 34.5 | 23.7 |
| 1 Mag Sep. 23.5 Min Grind | 4.88 | 72.8 | 34.3 | 24.9 |
| 5 Mag. Sep. 25 Min Grind | 4.04 | 66.5 | 74.2 | 49.3 |
| 0.089 lb Amine | 3.80 | 65.0 | | |
| 0.156 lb Amine | 3.55 | 56.1 | | |
| 0.222 lb Amine | 3.56 | 51.5 | 81.1 | 41.8 |
| 0.444 lb Amine | 3.48 | 34.8 | 94.0 | 32.7 |

Table 15

Initial Pellet Roasting Tests - Pellets Made with 16 % Na₂CO₃

Pellets from Flotation Concentrate using 0.222 lb Amine/LT

| Sample Description | Roast Temp, C | % Na ₂ CO ₃ | ppm V | ppm Na | ppm Si | Dry Ball Weight, g | Theo. V Conc, ppm | Leach %V Rec | Total %V Rec |
|----------------------|---------------|-----------------------------------|-------|--------|--------|--------------------|-------------------|--------------|--------------|
| 2 Pellets Flot Conc. | 900 | 16 | 17.05 | 84.76 | 3.59 | 3.5248 | 21.90 | 77.9 | 40.1 |
| 2 Pellets Flot Conc. | 950 | 16 | 16.20 | 75.26 | 5.62 | 3.2158 | 19.98 | 81.1 | 41.8 |
| 2 Pellets Flot Conc. | 1000 | 16 | 18.77 | 81.32 | 5.95 | 3.5569 | 22.10 | 85.0 | 43.8 |
| 2 Pellets Flot Conc. | 1050 | 16 | 18.48 | 69.15 | 6.01 | 3.3094 | 20.56 | 89.9 | 46.3 |

Pellets from Flotation Concentrate using 0.444 lb Amine/LT

| Sample Description | Roast Temp, C | % Na ₂ CO ₃ | ppm V | ppm Na | ppm Si | Dry Ball Weight, g | Theo. V Conc, ppm | Leach % V Rec | Total % V Rec |
|----------------------|---------------|-----------------------------------|-------|--------|--------|--------------------|-------------------|---------------|---------------|
| 2 Pellets Flot Conc. | 900 | 16 | 23.81 | 89.61 | 4.57 | 3.6826 | 25.69 | 92.7 | 32.2 |
| 2 Pellets Flot Conc. | 950 | 16 | 21.23 | 77.50 | 6.34 | 3.2371 | 22.58 | 94.0 | 32.7 |
| 2 Pellets Flot Conc. | 1000 | 16 | 22.03 | 82.13 | 6.51 | 3.3158 | 23.13 | 95.2 | 33.1 |
| 2 Pellets Flot Conc. | 1050 | 16 | 22.99 | 70.78 | 6.50 | 3.3836 | 23.60 | 97.4 | 33.9 |

Table 16

Final Pellet Product
Chemical Analysis

| %Fe | %SiO ₂ | %V ₂ O ₅ | %Na ₂ O | Calculated %Na ₂ CO ₃ |
|------|-------------------|--------------------------------|--------------------|--|
| 50.6 | 3.05 | 0.96 | 9.13 | 15.61 |

Chemical Analysis of
Final Flotation Product with 0.222 pounds Amine per Long Ton

| %Fe | %SiO ₂ | %V ₂ O ₅ |
|------|-------------------|--------------------------------|
| 59.6 | 3.56 | 1.08 |

Calculated Pellet Analysis
Using Flotation Concentrate Analysis and Assuming 16% Na₂CO₃

| %Fe | %SiO ₂ | %V ₂ O ₅ |
|------|-------------------|--------------------------------|
| 50.1 | 2.99 | 0.91 |

Pellet Leach Solutions

| Leach Solution Description | Vanadium Analysis (ppm) | Vanadium Theoretical V. (ppm) | Leach %V Rec | Total %V Rec |
|----------------------------|-------------------------------|-------------------------------------|-----------------|-----------------|
| 1000 grams Pellets/Liter | 3980 | 5378 | 74.0 | 38.1 |
| 3000 grams of Pellets/10 L | 1402 | 1613 | 86.9 | 44.8 |

Pellet Leach Pulp Analysis

| Starting Mass, g | Ending Mass, g | % Fe | % SiO ₂ | % V ₂ O ₅ | % Na ₂ O | Leach %V Rec. | Total %V Rec. |
|---------------------|-------------------|---------|-----------------------|------------------------------------|------------------------|------------------|------------------|
| 500 | 451.6 | 53.6 | 3.61 | 0.227 | 3.85 | 78.6 | 40.5 |
| 3000 | 2621.0 | 53.9 | 3.20 | 0.122 | 3.65 | 88.9 | 45.8 |

Table 17

| Red Cake Precipitation | | | | | | | |
|------------------------|---------|-----------------------|------------------------------------|------------------------|----------|-----------|-----------|
| Description | % Fe | % SiO ₂ | % V ₂ O ₅ | % Na ₂ O | ppm V | ppm Na | ppm Si |
| Precipitate 1 | 0.42 | 0.11 | 74.5 | 7.8 | | | |
| Solution Feed 1 | | | | | 9567 | 84850 | 255.0 |
| Solution Filtrate 1 | | | | | 69 | | 86.2 |
| Precipitate 2 | 0.20 | 0.52 | 78.2 | 10.0 | | | |
| Solution Feed 2 | | | | | 3980 | 35150 | 555 |
| Solution Filtrate 2 | | | | | 61.8 | 26700 | 529 |
| Precipitate 3 | 0.15 | 0.56 | 77.8 | 9.8 | | | |
| Solution Feed 3 | | | | | 1402 | 11945 | 179 |
| Solution Filtrate 3 | | | | | 102 | 9562 | 162 |

Analysis of Roasted Precipitate
Roasts Performed at 1000 C

| Description | % Fe | % SiO ₂ | % V ₂ O ₅ | % Na ₂ O | %Vanadium Recovered from Leach | Total % V Recovered |
|---------------|---------|-----------------------|------------------------------------|------------------------|--------------------------------------|------------------------|
| Precipitate 1 | 0.19 | 0.09 | 92.3 | 6.52 | 99.3 | 37.8 |
| Precipitate 2 | 0.08 | 0.22 | 90.2 | 8.87 | 98.4 | 37.5 |
| Precipitate 3 | 0.08 | 0.23 | 90.3 | 8.81 | 92.7 | 41.5 |

Table 18

Initial Ion-Exchange Tests
Testing was Performed at pH 7

| Resin Description | Resin (g) | V Sol. (ml) | Total ug V | ugV/gRes Absorbed | mmoles/g Resin | ug/ml V | ug/ml Na | ug/ml Si |
|-------------------|-----------|-------------|------------|-------------------|----------------|---------|----------|----------|
| Feed Solution | | | | | | 20.29 | 85.7 | 10.0 |
| Feed Solution | | | | | | 20.17 | 84.8 | 10.0 |
| Amberlite | 10.00 | 50 | 1011 | 28.3 | 0.0006 | 14.56 | 276.7 | 10.1 |
| Amberlite | 5.00 | 50 | 1011 | 17.2 | 0.0003 | 18.51 | 161.9 | 10.1 |
| Diaion WA30 | 10.00 | 50 | 1011 | 101.0 | 0.0020 | 0.02 | 81.9 | 2.9 |
| Diaion WA30 | 5.00 | 50 | 1011 | 202.1 | 0.0040 | 0.02 | 86.2 | 3.1 |
| Diaion WA30 | 2.00 | 50 | 1011 | 489.2 | 0.0096 | 0.66 | 80.4 | 9.3 |
| Diaion WA30 | 2.00 | 100 | 2023 | 838.8 | 0.0165 | 3.45 | 81.4 | 9.7 |
| Diaion WA30 | 0.50 | 50 | 1011 | 1482.6 | 0.0291 | 5.40 | 85.4 | 9.1 |
| Dow 1 | 10.00 | 50 | 1011 | 101.0 | 0.0020 | 0.02 | 91.0 | 3.1 |
| Dow 1 | 5.00 | 50 | 1011 | 202.1 | 0.0040 | 0.02 | 87.2 | 0.6 |
| Dow 1 | 2.00 | 50 | 1011 | 505.0 | 0.0099 | 0.03 | 79.4 | 8.1 |
| Dow 1 | 2.00 | 100 | 2023 | 1010.4 | 0.0198 | 0.02 | 78.8 | 8.3 |
| Dow 1 | 0.50 | 50 | 1011 | 2015.5 | 0.0396 | 0.07 | 89.2 | 1.9 |
| Dow 1 | 0.50 | 100 | 2023 | 3876.3 | 0.0761 | 0.85 | 84.8 | 3.6 |
| Dow 1 | 0.10 | 50 | 1011 | 6454.9 | 0.1267 | 7.32 | 84.0 | 9.0 |
| Dow 1 | 0.05 | 50 | 1011 | 6261.7 | 0.1229 | 13.97 | 86.3 | 12.8 |
| Dow 2 | 10.00 | 50 | 1011 | 100.9 | 0.0020 | 0.04 | 86.8 | 7.0 |
| Dow 2 | 5.00 | 50 | 1011 | 202.1 | 0.0040 | 0.02 | 90.0 | 6.7 |
| Dow 2 | 2.00 | 50 | 1011 | 505.2 | 0.0099 | 0.02 | 81.9 | 7.2 |
| Dow 2 | 2.00 | 100 | 2023 | 1010.4 | 0.0198 | 0.02 | 81.1 | 6.9 |
| Dow 2 | 0.50 | 50 | 1011 | 2020.9 | 0.0397 | 0.02 | 82.0 | 6.7 |
| Dow 2 | 0.50 | 100 | 2023 | 4041.9 | 0.0793 | 0.02 | 87.8 | 7.0 |
| Dow 2 | 0.10 | 50 | 1011 | 9750.0 | 0.1914 | 0.73 | 85.9 | 10.2 |
| Dow 2 | 0.05 | 50 | 1011 | 16096.0 | 0.3160 | 4.13 | 85.1 | 11.2 |

Table 19
Ion-Exchange Capacities

| Sample Description | ppm V | Capacity mmoles/g | *Calc. mmoles/g | Resin Type |
|------------------------------|-------|-------------------|-----------------|------------------------|
| Amberlite | 18.51 | 0.0003 | | Cation Strongly Acidic |
| Amberlite | 14.56 | 0.0006 | | Cation Strongly Acidic |
| Amberlite Estimated Capacity | | | 0.0006 | |
| Dow 1 | 0.02 | 0.0020 | 0.0132 | Anion Strongly Basic |
| Dow 1 | 0.02 | 0.0040 | 0.0132 | Anion Strongly Basic |
| Dow 1 | 0.03 | 0.0099 | 0.0143 | Anion Strongly Basic |
| Dow 1 | 0.02 | 0.0198 | 0.0132 | Anion Strongly Basic |
| Dow 1 | 0.07 | 0.0396 | 0.0194 | Anion Strongly Basic |
| Dow 1 | 0.85 | 0.0761 | 0.0787 | Anion Strongly Basic |
| Dow 1 | 7.32 | 0.1267 | 0.1245 | Anion Strongly Basic |
| Dow 1 | 13.97 | 0.1229 | 0.1245 | Anion Strongly Basic |
| *Dow 1 Calculated Capacity | | | 0.1245 | |
| Dow 2 | 0.04 | 0.0020 | 0.0320 | Anion Strongly Basic |
| Dow 2 | 0.02 | 0.0040 | 0.0249 | Anion Strongly Basic |
| Dow 2 | 0.02 | 0.0099 | 0.0249 | Anion Strongly Basic |
| Dow 2 | 0.02 | 0.0198 | 0.0249 | Anion Strongly Basic |
| Dow 2 | 0.02 | 0.0397 | 0.0247 | Anion Strongly Basic |
| Dow 2 | 0.02 | 0.0793 | 0.0246 | Anion Strongly Basic |
| Dow 2 | 0.73 | 0.1914 | 0.1893 | Anion Strongly Basic |
| Dow 2 | 4.13 | 0.3160 | 0.3164 | Anion Strongly Basic |
| *Dow 2 Calculated Capacity | | | 0.3189 | |
| Diaion WA30 | 0.02 | 0.0020 | 0.0036 | Anion Weakly Basic |
| Diaion WA30 | 0.02 | 0.0040 | 0.0036 | Anion Weakly Basic |
| Diaion WA30 | 0.66 | 0.0096 | 0.0070 | Anion Weakly Basic |
| Diaion WA30 | 3.45 | 0.0165 | 0.0200 | Anion Weakly Basic |
| Diaion WA30 | 5.40 | 0.0291 | 0.0273 | Anion Weakly Basic |
| *Diaion Calculated Capacity | | | 0.0650 | |

*Note: The calculated capacity of the ion-exchange resin is accomplished by running a computer reiteration program and determining the best fit for an equation of the form
 $Capacity = B + m \cdot e^{-k(V)}$ where B, m, and k are calculated constants and V is the concentration of vanadium remaining in solution. The calculated capacity is equal to B when the concentration of Vanadium is at infinity. The calculated equations are listed below.

| Resin Description | B | m | k | R ² |
|-----------------------------|---------|----------|--------|----------------|
| *Dow 1 Calculated Capacity | 0.12453 | -0.11373 | 1.074 | 0.98 |
| *Dow 2 Calculated Capacity | 0.31890 | -0.30086 | 1.156 | 0.97 |
| *Diaion Calculated Capacity | 0.06496 | -0.06151 | -0.090 | 0.97 |

Table 20

Ion-Exchange Capacities of Resins with Changing pH

Initial Vanadium Solution = 140 ug/ml
 Volume of Vanadium Solution = 100 ml
 Mass of Ion-exchange Resin = 2.00 grams

| Sample | | ug V/ ml | ug V/ml Absorbed | pH | mmoles V/ g Resin |
|--------|------|-------------|---------------------|------|----------------------|
| Diaion | WA30 | 98.6 | 41.4 | 11.3 | 0.0406 |
| Diaion | WA30 | 93.6 | 46.4 | 10.0 | 0.0456 |
| Diaion | WA30 | 67.6 | 72.4 | 7.0 | 0.0710 |
| Diaion | WA30 | 57.9 | 82.1 | 5.0 | 0.0806 |
| Dow 1 | | 33.2 | 106.8 | 11.3 | 0.1049 |
| Dow 1 | | 45.7 | 94.3 | 10.0 | 0.0926 |
| Dow 1 | | 65.1 | 74.9 | 7.0 | 0.0735 |
| Dow 1 | | 72.7 | 67.3 | 5.0 | 0.0660 |
| Dow 2 | | 18.3 | 121.7 | 11.3 | 0.1194 |
| Dow 2 | | 11.8 | 128.2 | 10.0 | 0.1258 |
| Dow 2 | | 18.5 | 121.5 | 7.0 | 0.1193 |
| Dow 2 | | 34.7 | 105.3 | 5.0 | 0.1033 |

Table 21

Ion-Exchange Capacities with Precipitate Filtrate
 Precipitate Solution = 66 ug V/ml and pH 2.5

| Resin Description | ug V/ ml | Resin grams | ml of V Solution | mmoles V/ g Resin |
|----------------------|-------------|----------------|---------------------|----------------------|
| Dow 1 | 51.7 | 0.25 | 38 | 0.0425 |
| Dow 2 | 58.7 | 0.10 | 50 | 0.0712 |
| Diaion WA30 | 17.9 | 0.50 | 25 | 0.0472 |

Table 22

Solvent Extraction with Aliquat 336
100 Milliliters of 1400 ug V/ml Pellet Leach Solution

| Solvent Description | ug V/ ml Solute | Solvent Vol (ml) | g V/ml Solvent | % V Extracted | pH | Ratio of Solv.:Solute |
|---------------------|--------------------|------------------|-------------------|------------------|------|--------------------------|
| Aliquat 336 | 1009.0 | 10 | 0.0039 | 28 | 12.5 | 1 to 10 |
| Aliquat 336 | 979.1 | 20 | 0.0021 | 30 | 12.5 | 1 to 5 |
| Aliquat 336 | 903.4 | 40 | 0.0012 | 35 | 12.5 | 2 to 5 |
| Aliquat 336 | 336.7 | 10 | 0.0106 | 76 | 10 | 1 to 10 |
| Aliquat 336 | 290.7 | 20 | 0.0055 | 79 | 10 | 1 to 5 |
| Aliquat 336 | 288.7 | 40 | 0.0028 | 79 | 10 | 2 to 5 |
| Aliquat 336 | 48.6 | 10 | 0.0135 | 97 | 7 | 1 to 10 |
| Aliquat 336 | 36.1 | 20 | 0.0068 | 97 | 7 | 1 to 5 |
| Aliquat 336 | 32.8 | 40 | 0.0034 | 98 | 7 | 2 to 5 |
| Aliquat 336 | 2.3 | 10 | 0.0140 | 100 | 4.5 | 1 to 10 |
| Aliquat 336 | 2.4 | 20 | 0.0070 | 100 | 4.5 | 1 to 5 |
| Aliquat 336 | 1.4 | 40 | 0.0035 | 100 | 4.5 | 2 to 5 |

Table 23

Solvent Extraction with Aliquat 336
 Extraction of Filtrate from Red Cake Precipitation

| Solvent Description | ug V/ ml | Solvent Vol (ml) | mg V/ml Solvent | % V Extracted | pH | Ratio of Solv.:Solute |
|---------------------|-------------|------------------|--------------------|------------------|-----|--------------------------|
| Feed | 66.0 | | | | | |
| Extr Sol | 1.2 | 30 | 0.162 | 98 | 2.5 | 2 to 5 |

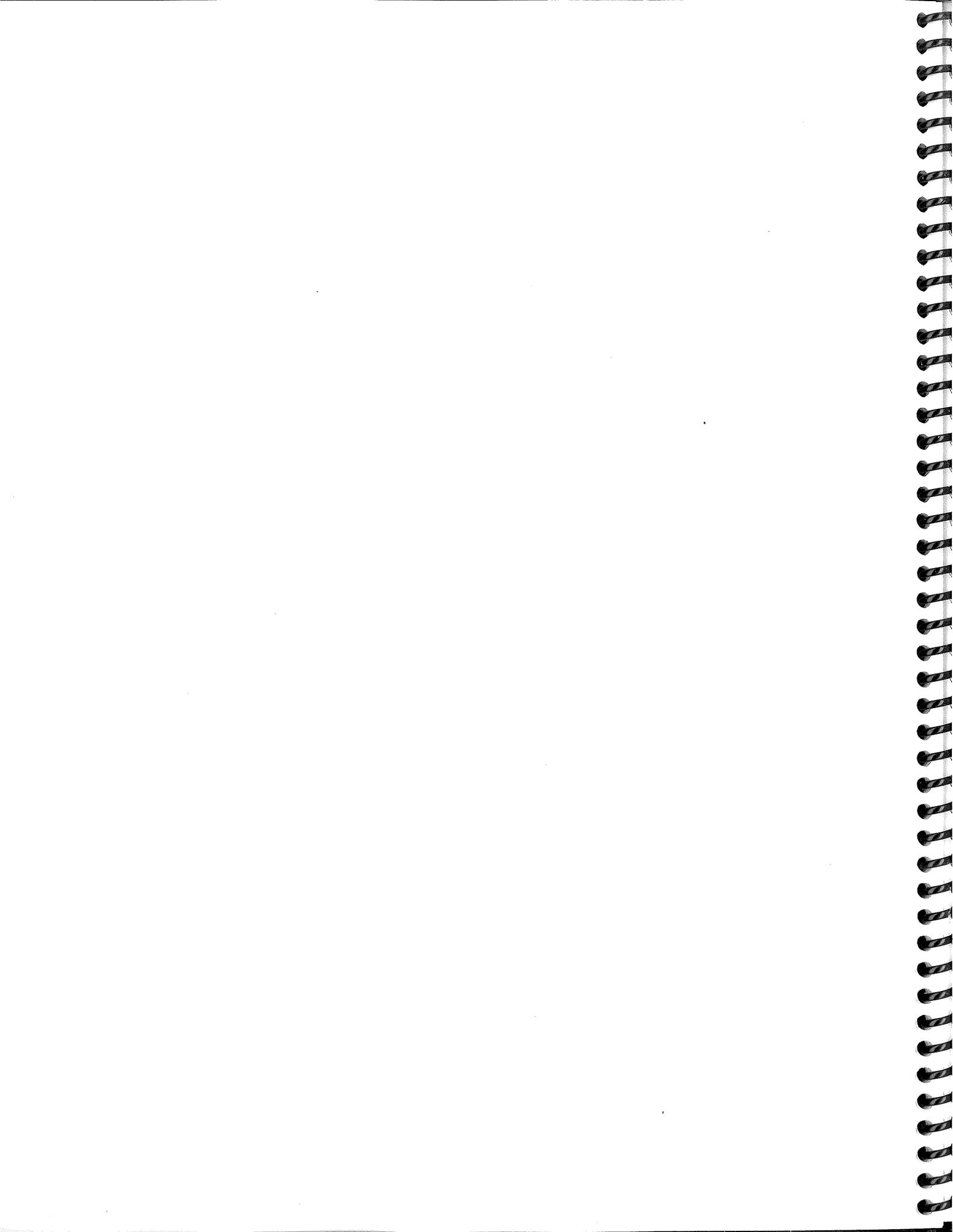


Figure 1

Vanadium Liberation Grinds

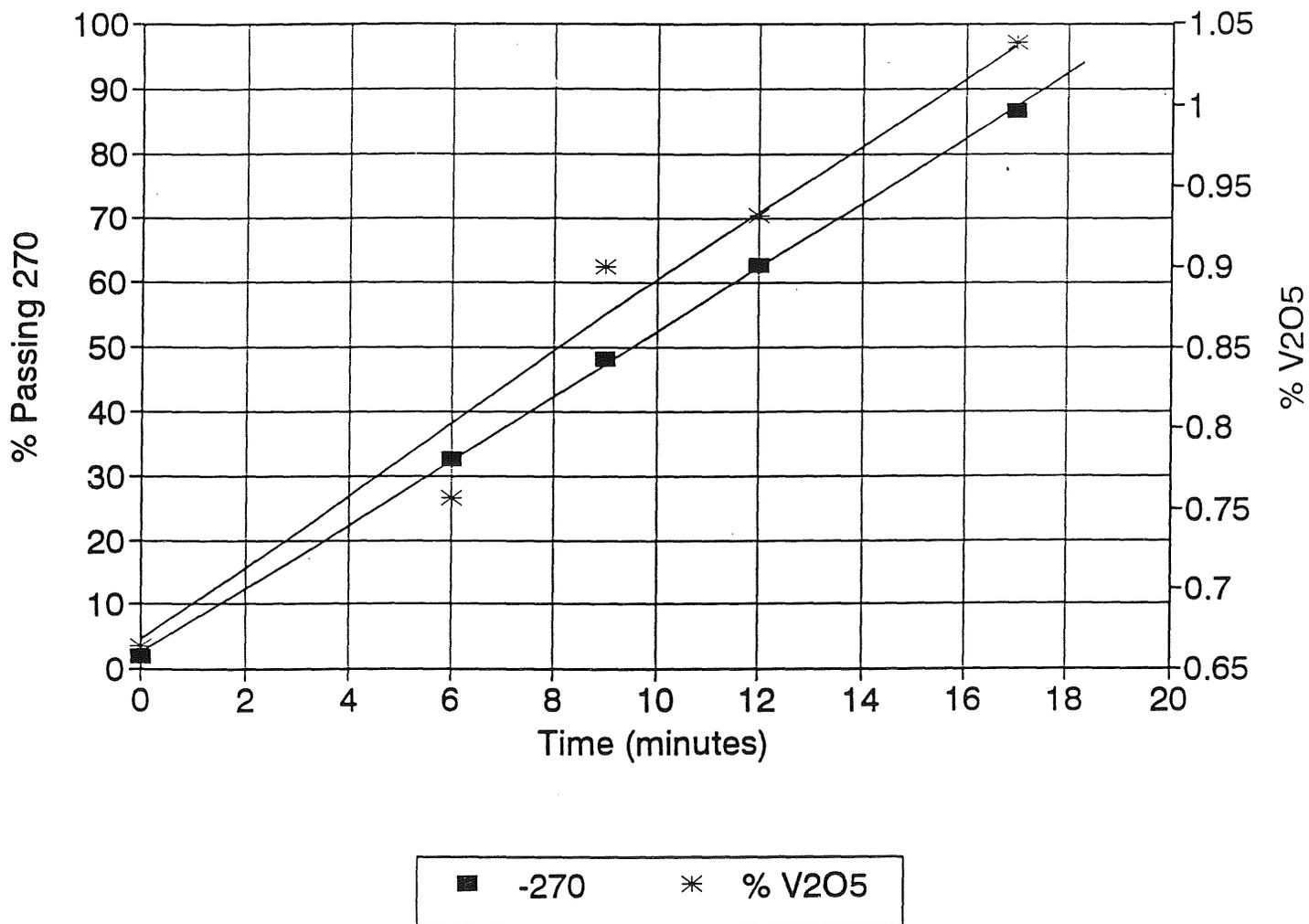


Figure 2

Silica Liberation Grinds

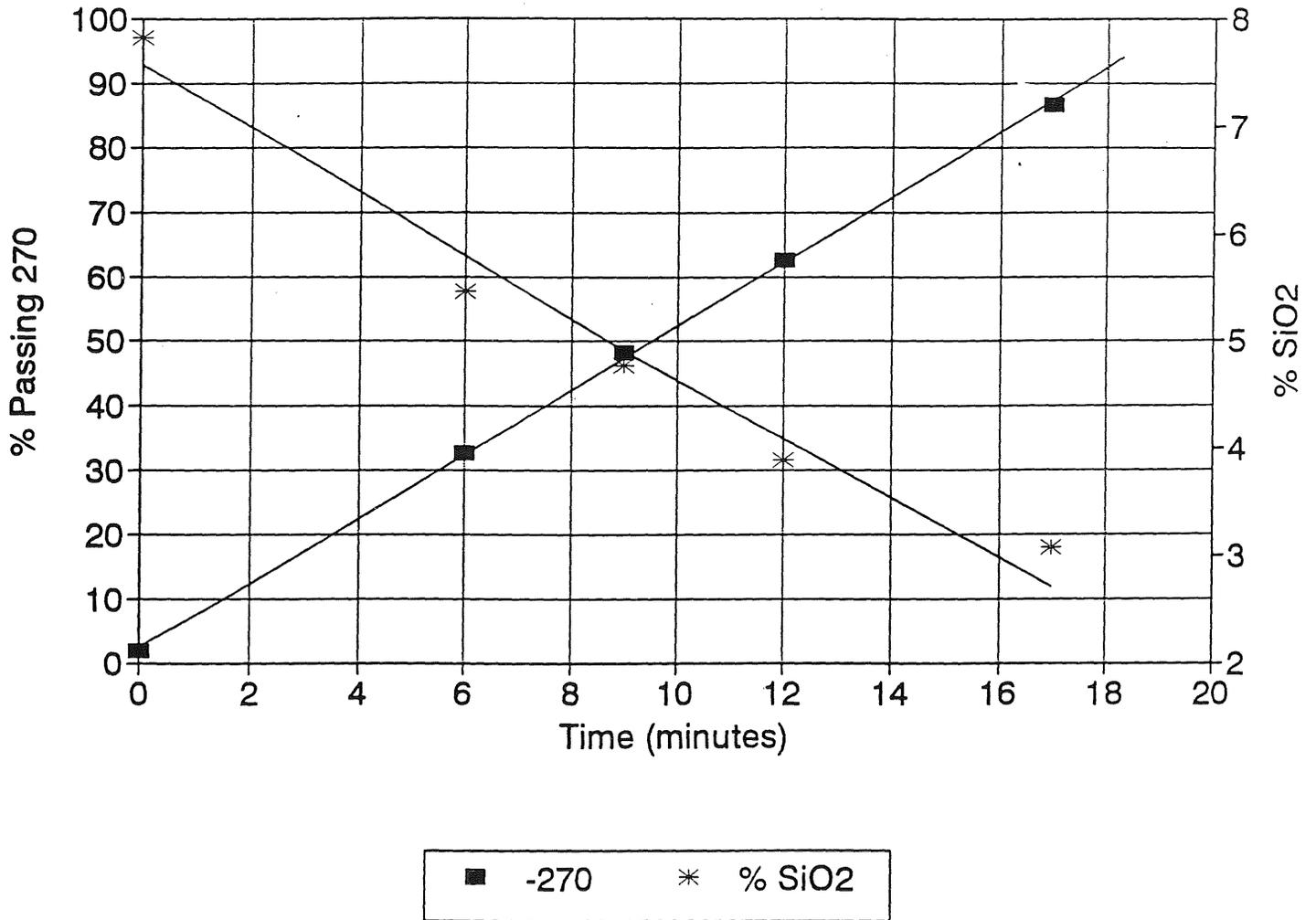


Figure 3

Silica and V2O5 vs % Passing -270 mesh

Davis Tube Data

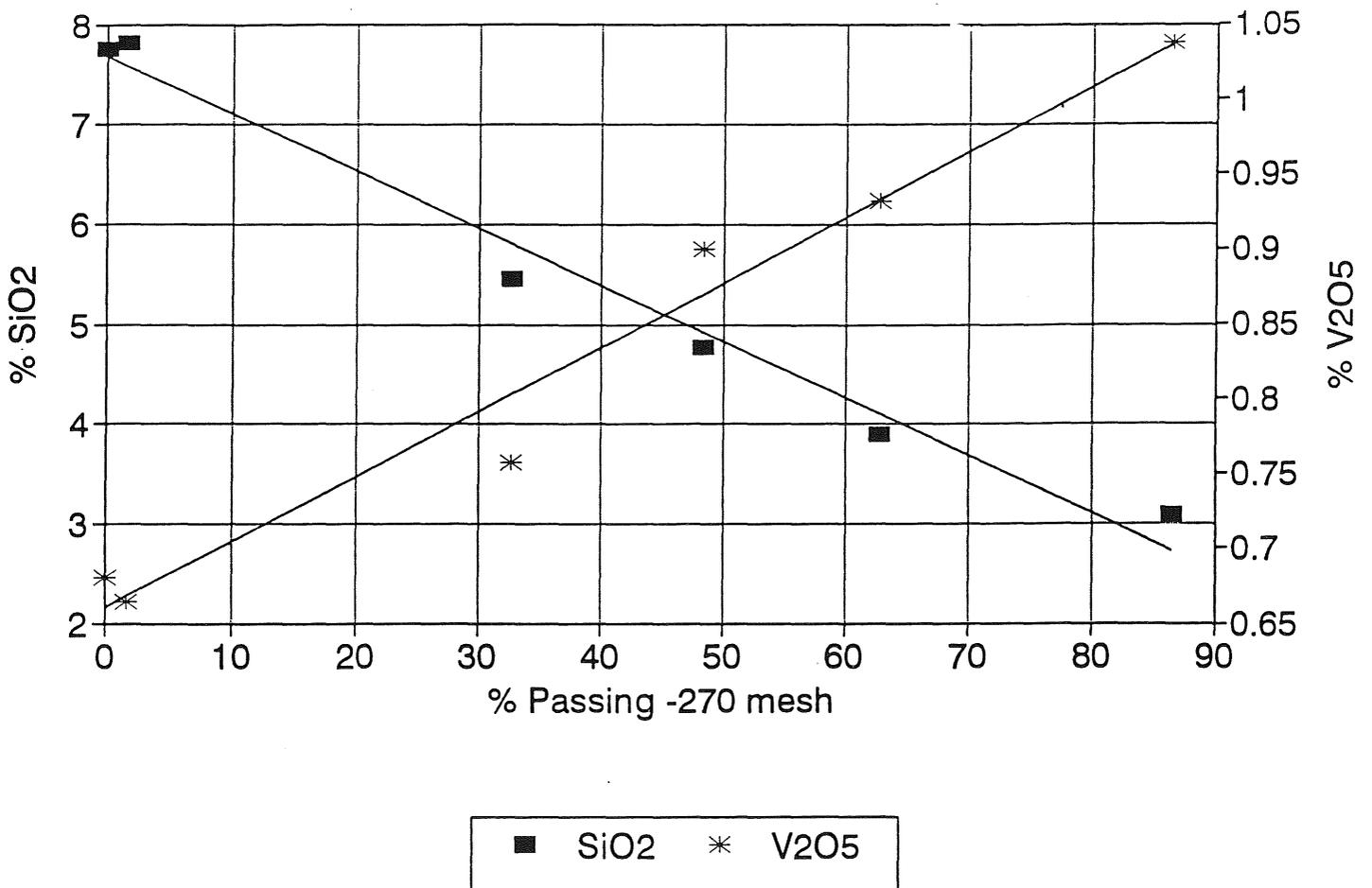


Figure 4

Liberation Grinds - Davis Tube Data

DT Silica vs DT V2O5

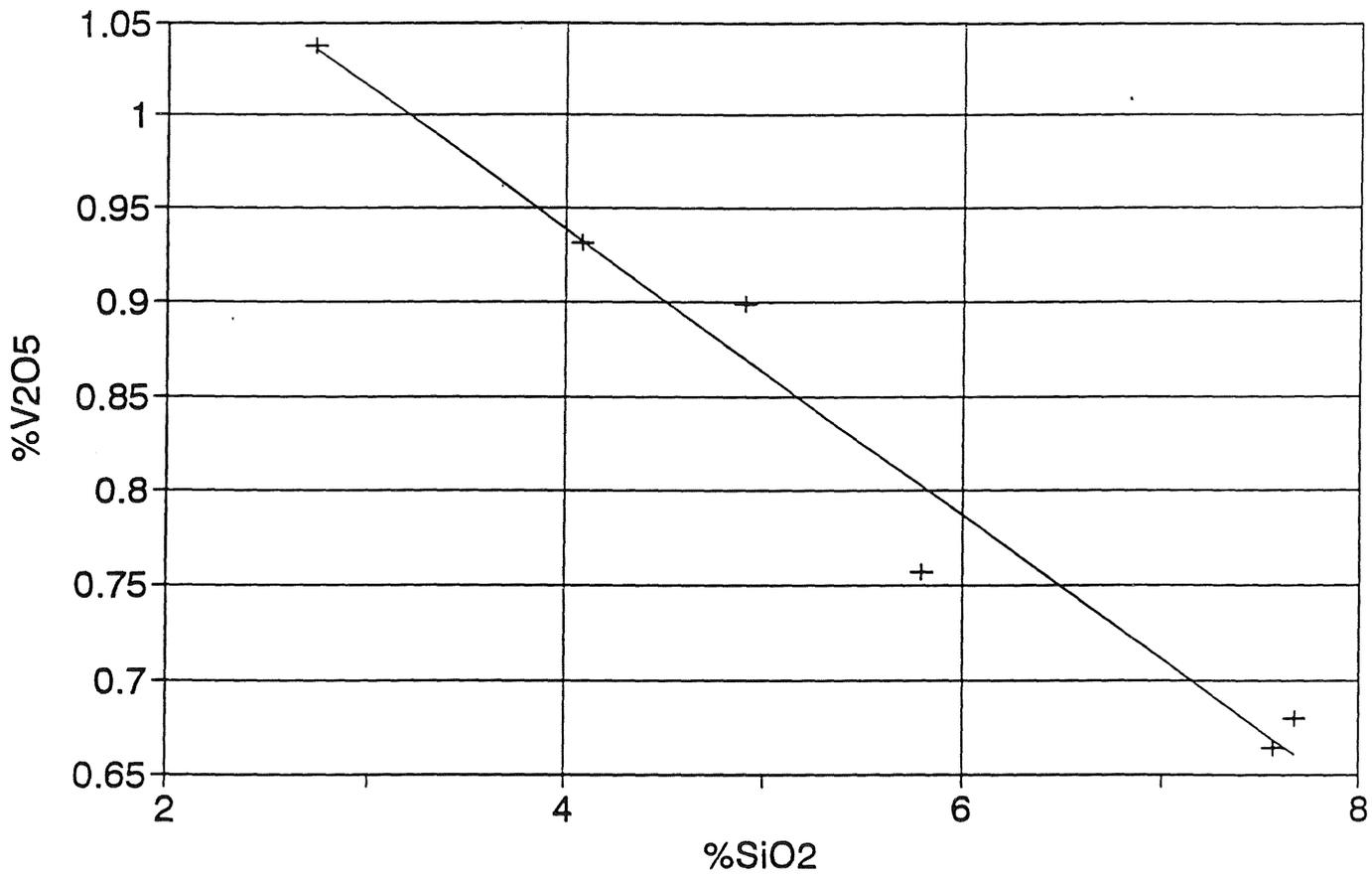


Figure 5

Liberation Grinds & Ball Mill Grinds

-270 Mesh Data

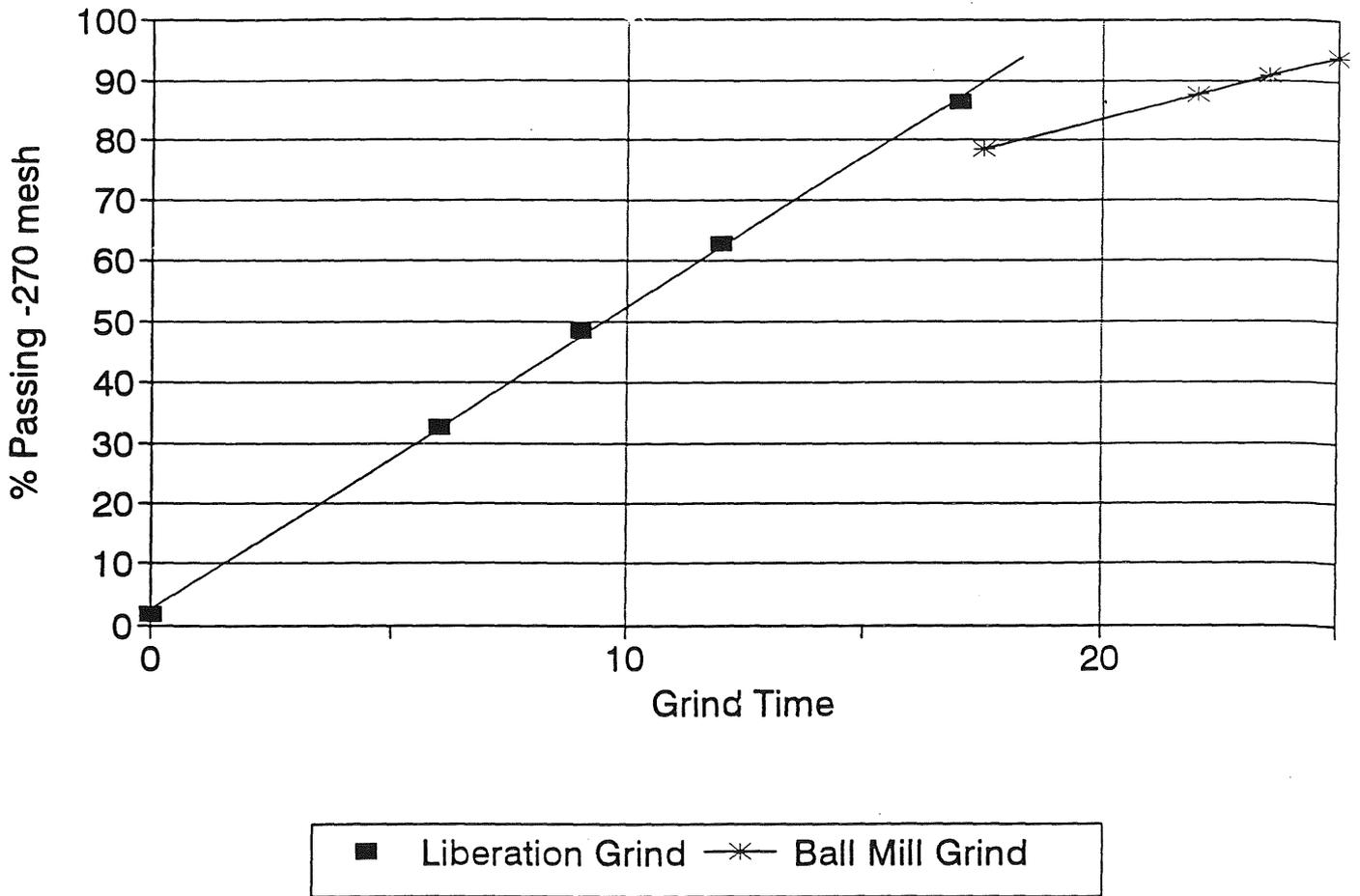


Figure 6

Ball Mill Grind for SiO₂ Liberation

Davis Tube Magnetic Concentrate

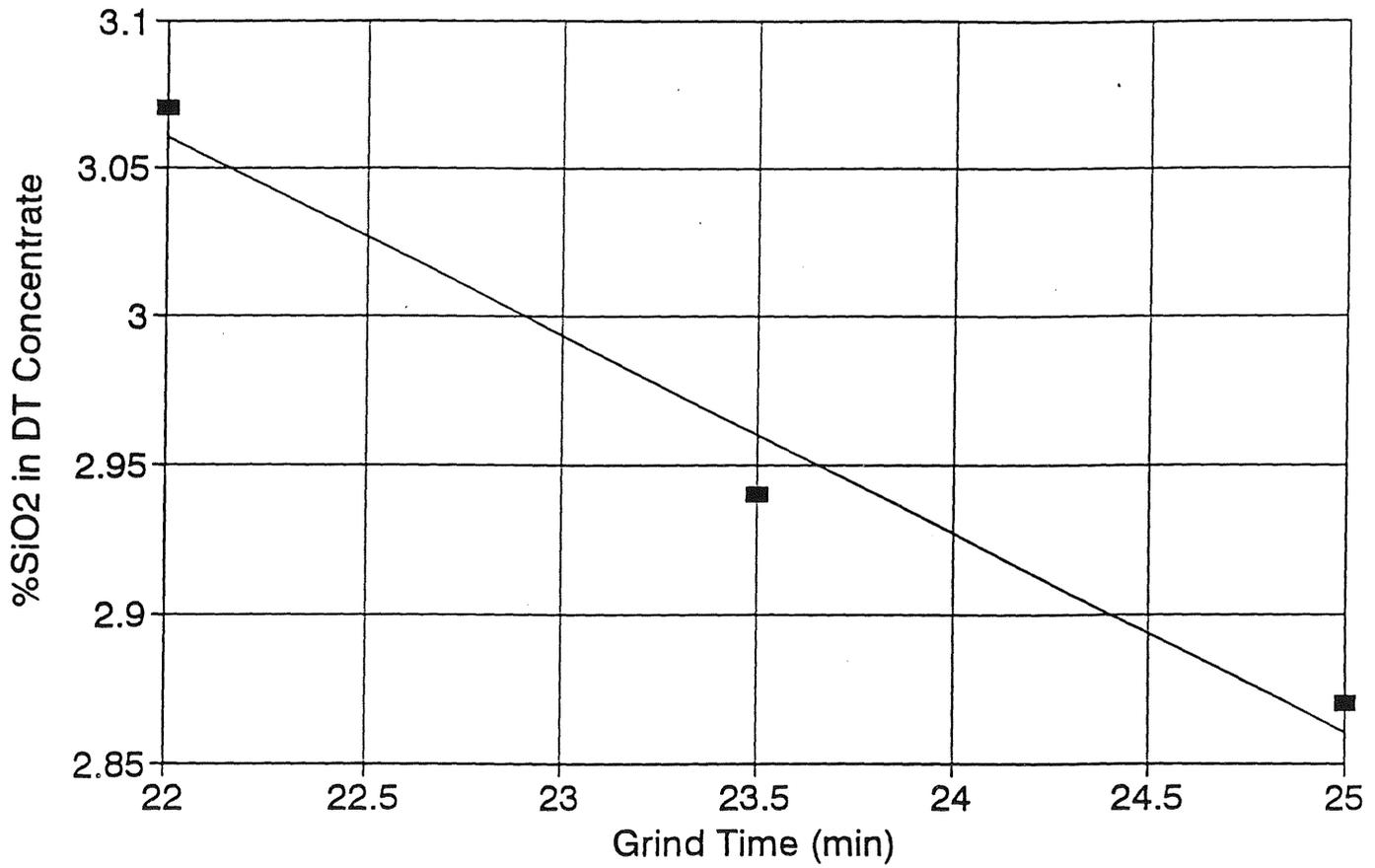


Figure 7

Ball Mill Grind for V2O5 Liberation

Davis Tube Magnetic Concentrate

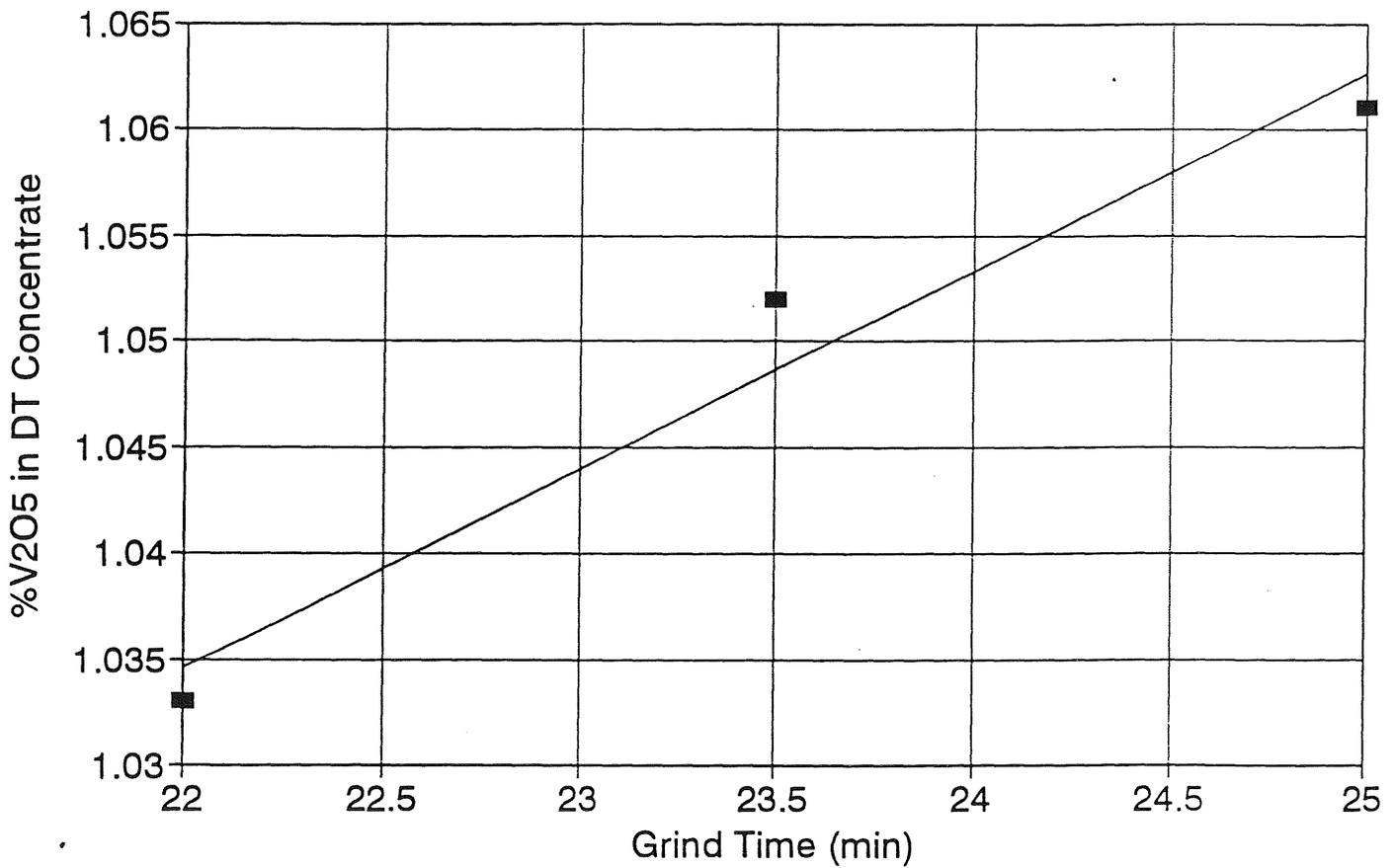


Figure 8

Drum Magnetic Separation - SiO₂ & V₂O₅

Sample Passed through Drum Separator

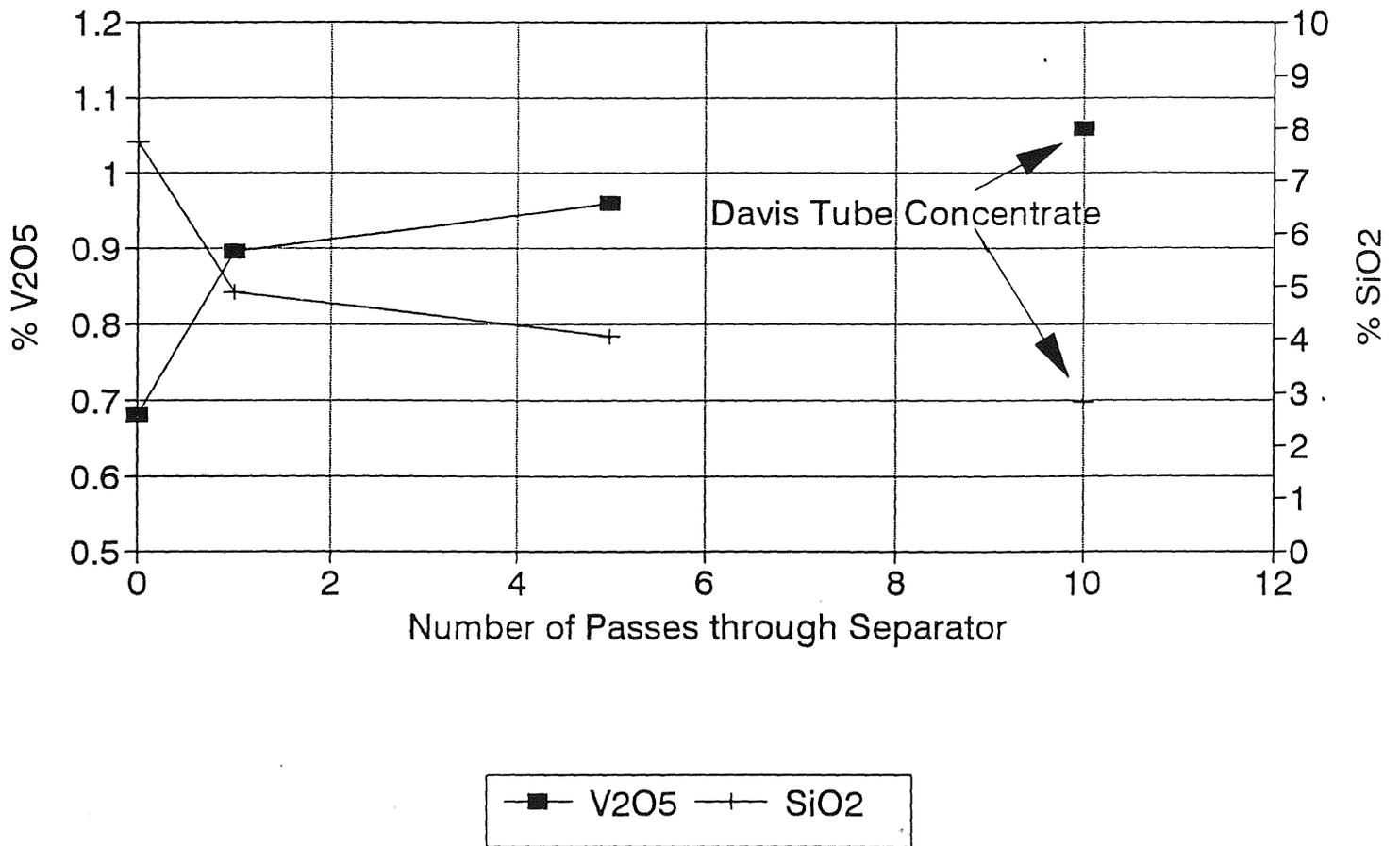


Figure 9

Iron by Size

Ball Mill Discharge vs Magnetic Conc.

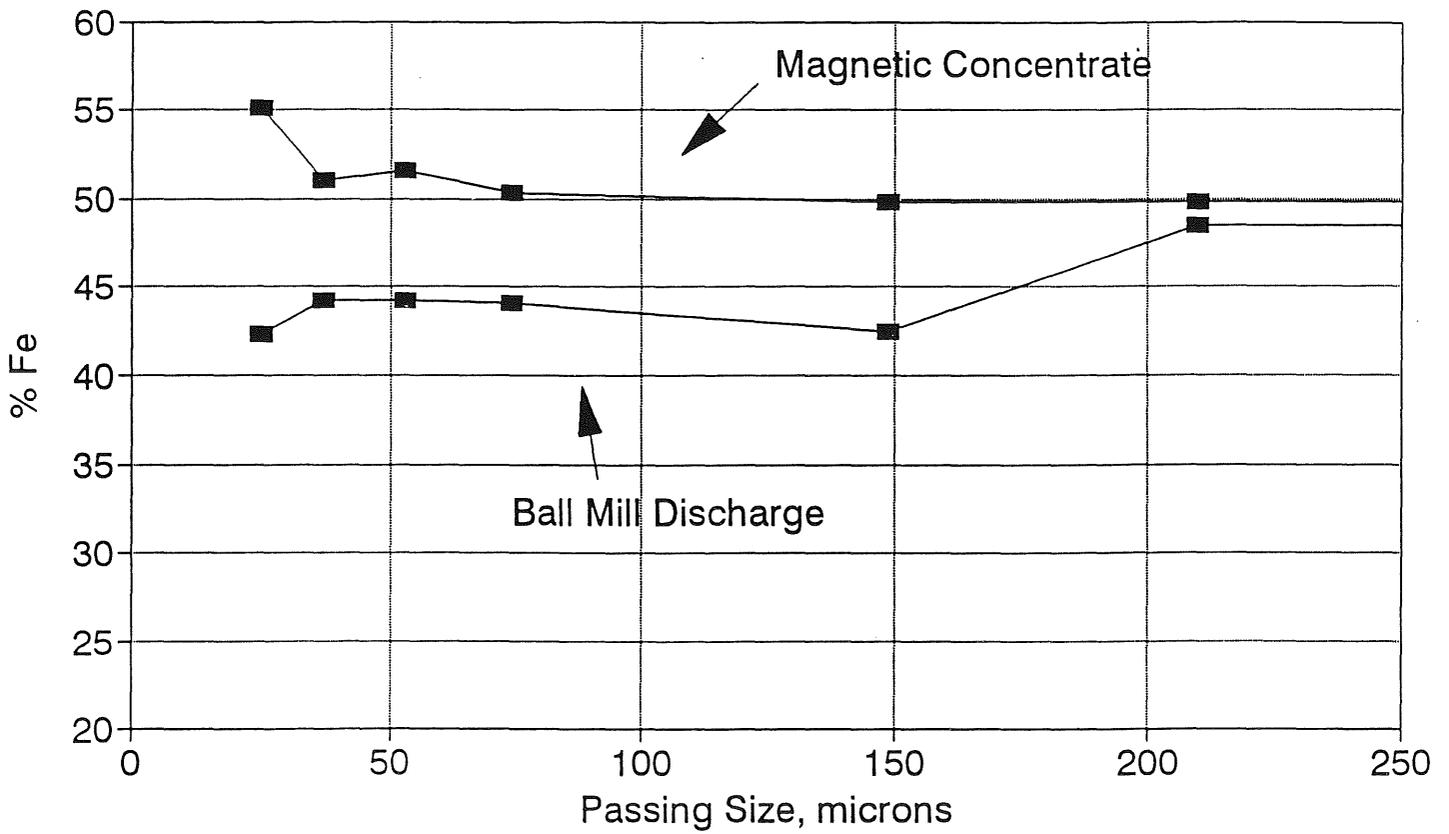


Figure 10

Silica by Size

Ball Mill Discharge vs Magnetic Conc.

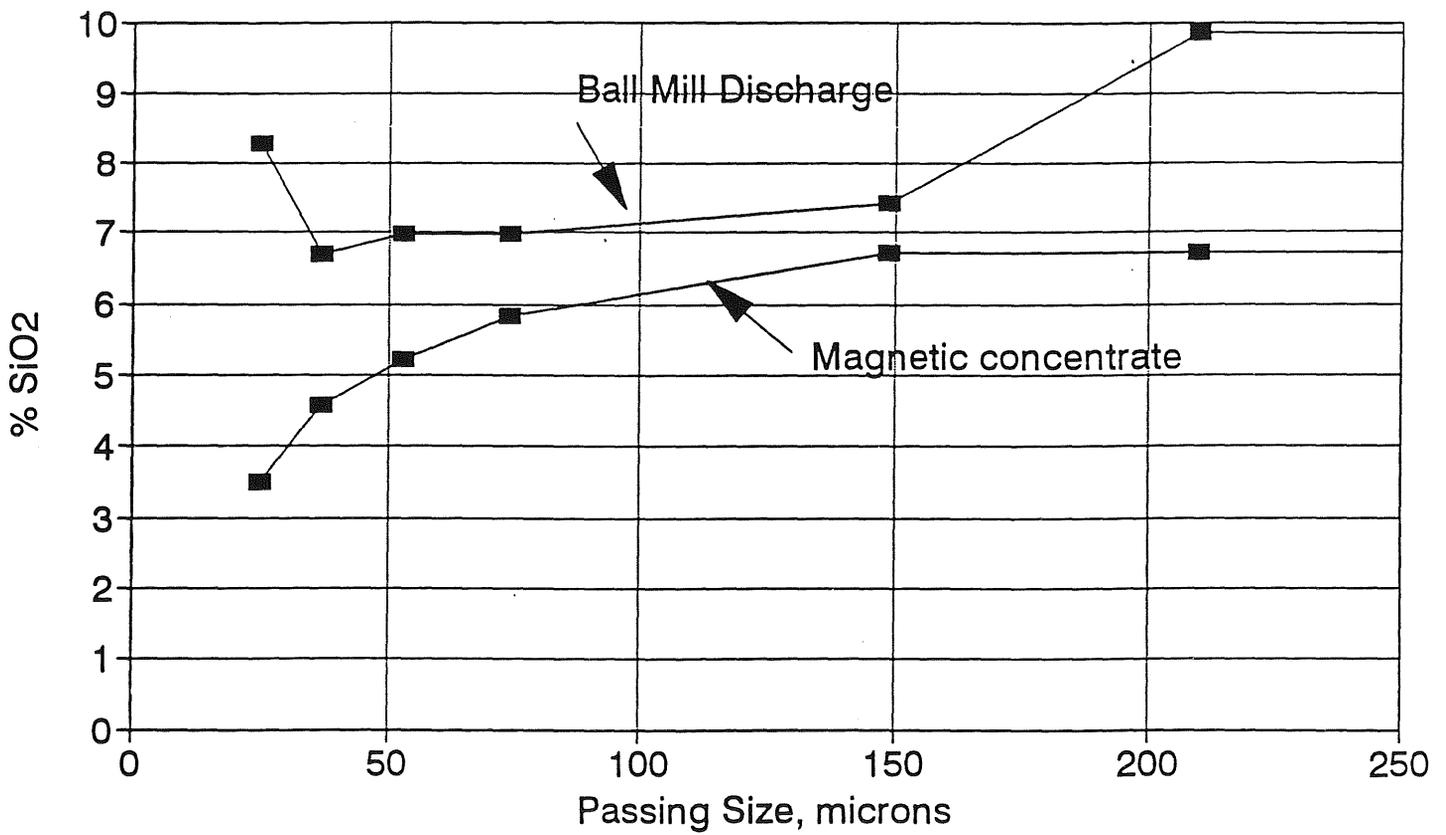


Figure 11

V2O5 by Size

Ball Mill Discharge vs Magnetic Conc.

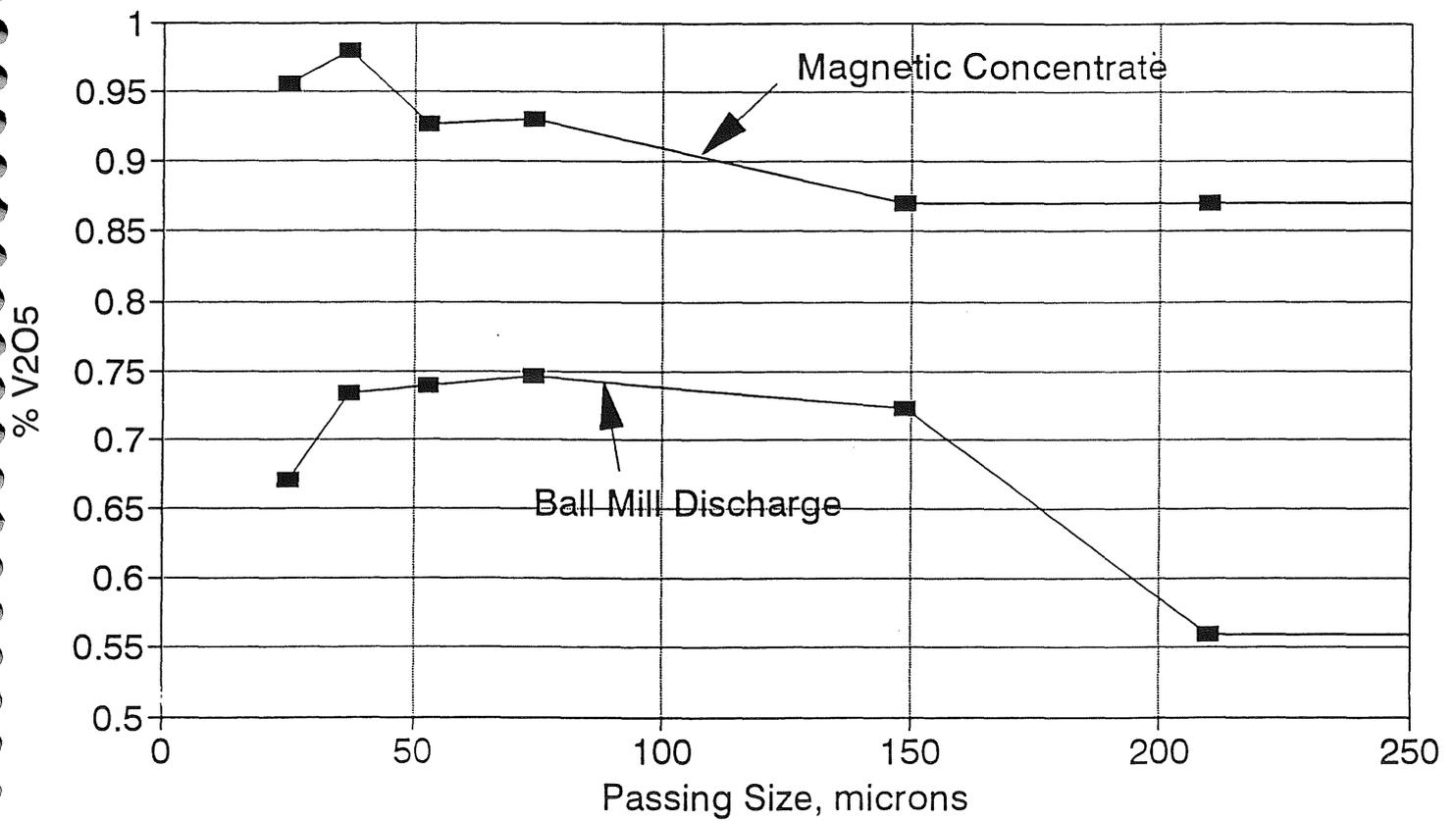
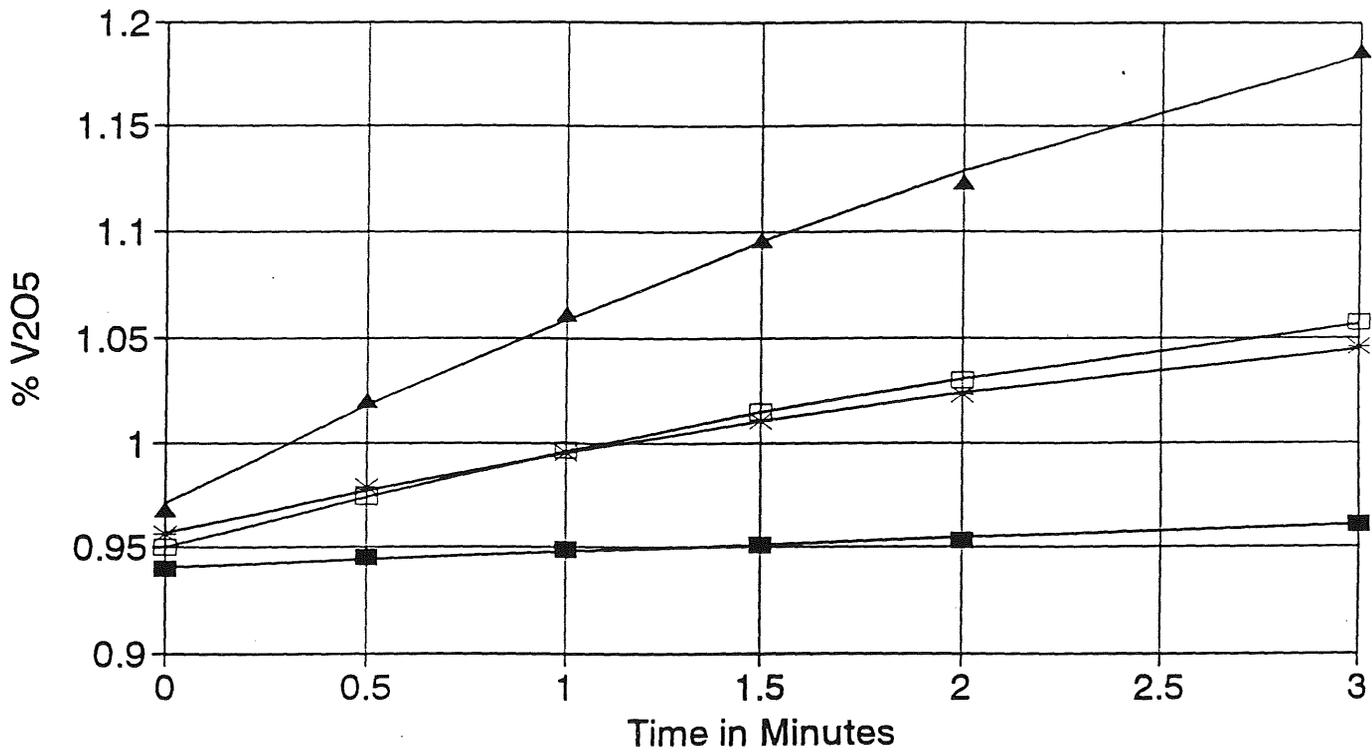


Figure 12

Percent V2O5 in Conc. vs Time

Rate Equation $C = C_f + (m \cdot e^{-kt})$

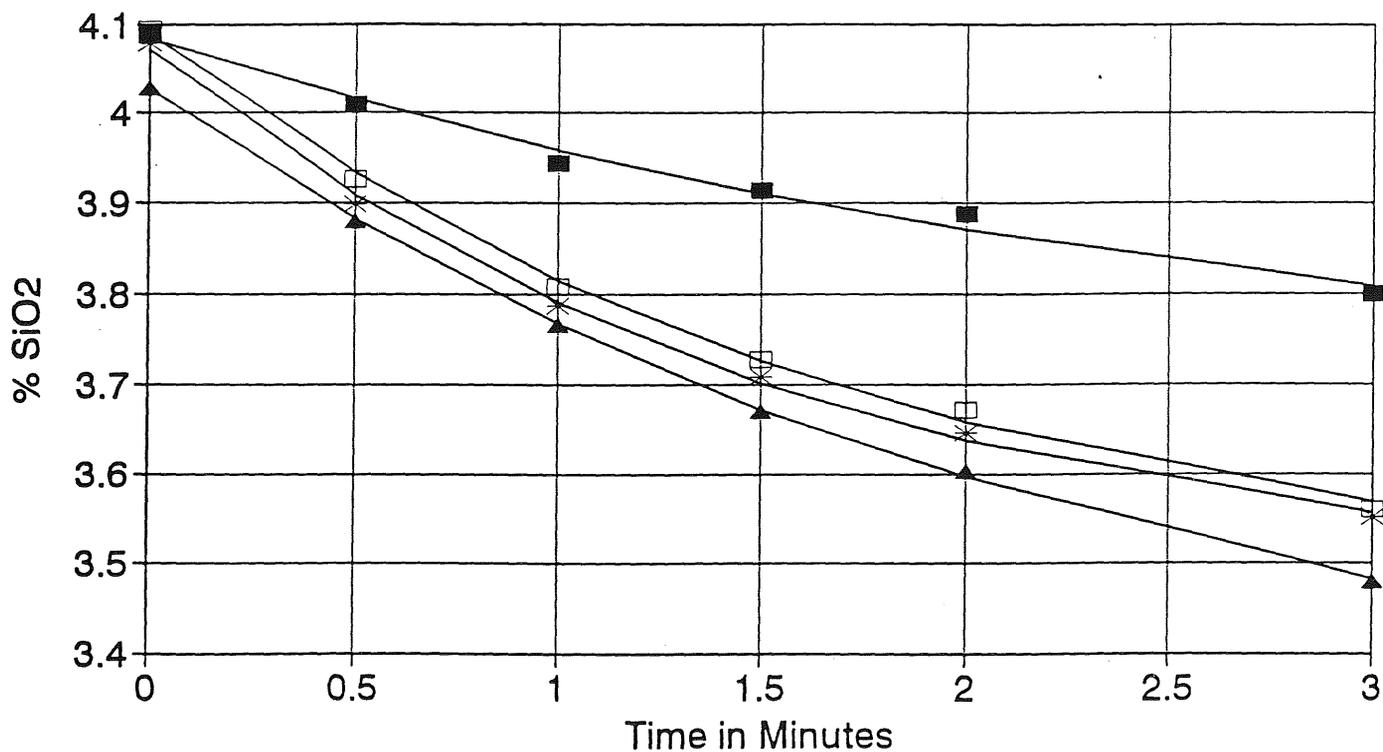


■ 0.089 lb Amin * 0.156 lb Amin □ 0.222 lb Amin ▲ 0.444 lb Amin

Figure 13

Percent Silica in Conc. vs Time

Rate Equation $C = C_f + (m \cdot e^{-kt})$



■ 0.089 lb Amin * 0.156 lb Amin □ 0.222 lb Amin ▲ 0.444 lb Amin

Figure 14

Amine Use vs Vandium Recovery

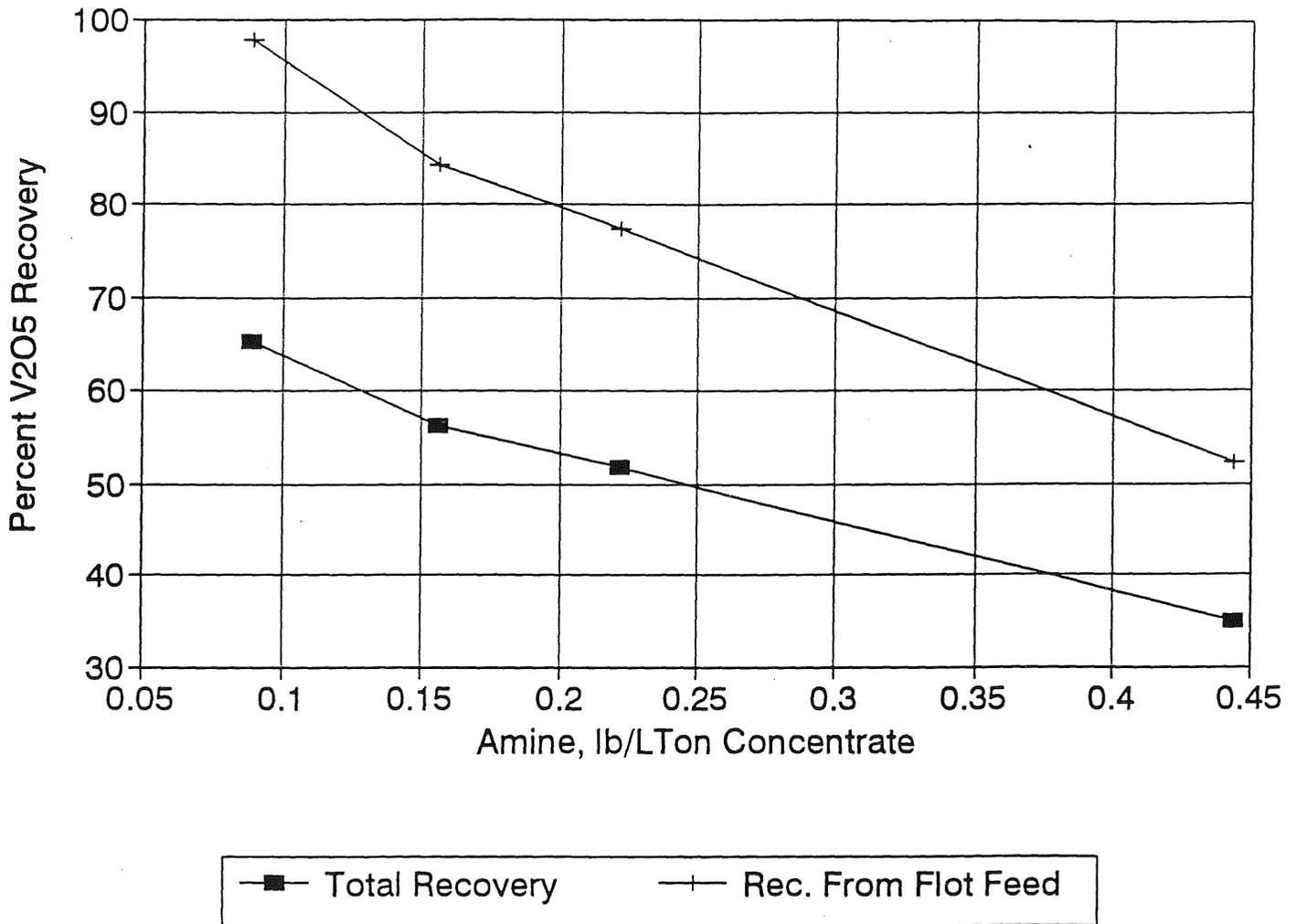
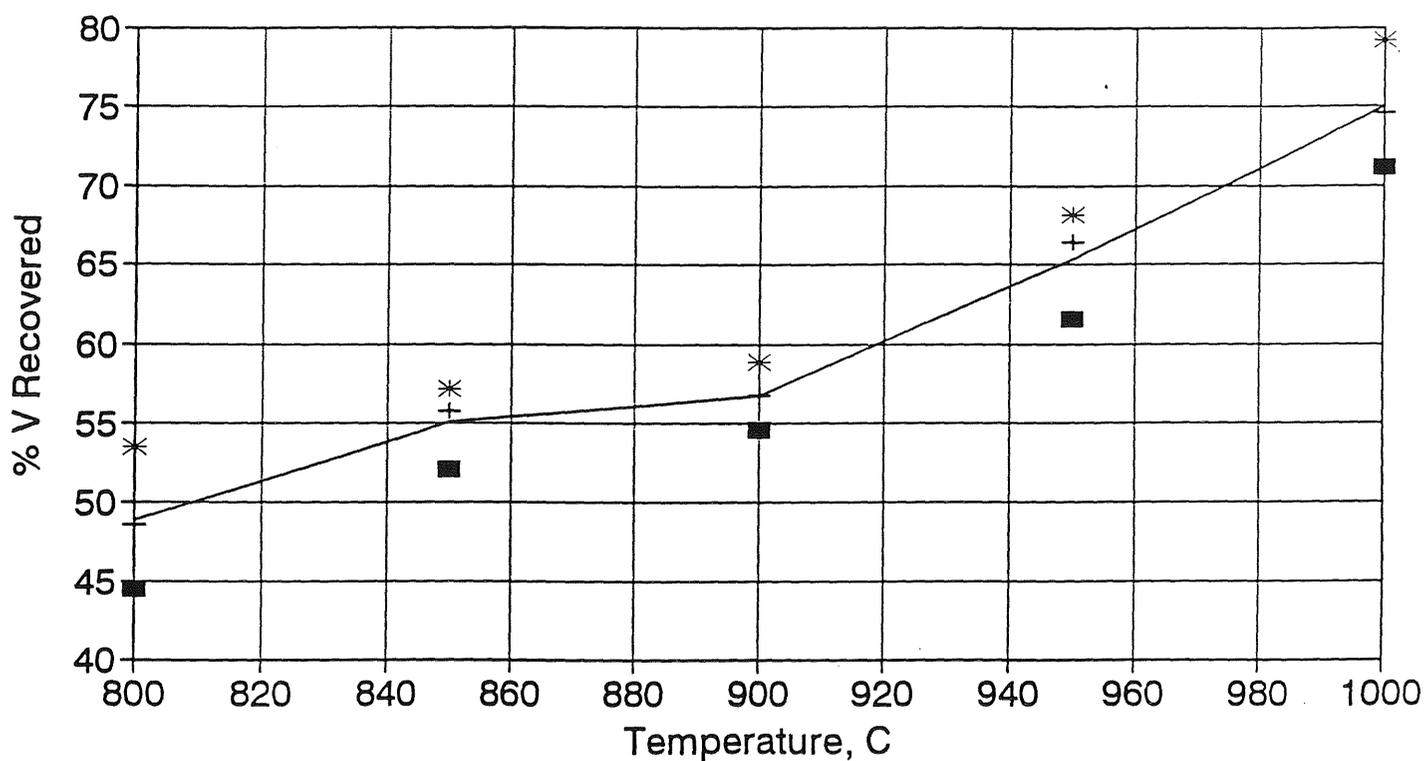


Figure 15

Sodium Chloride Roast Results

Recovery Based on V in Roasted Sample

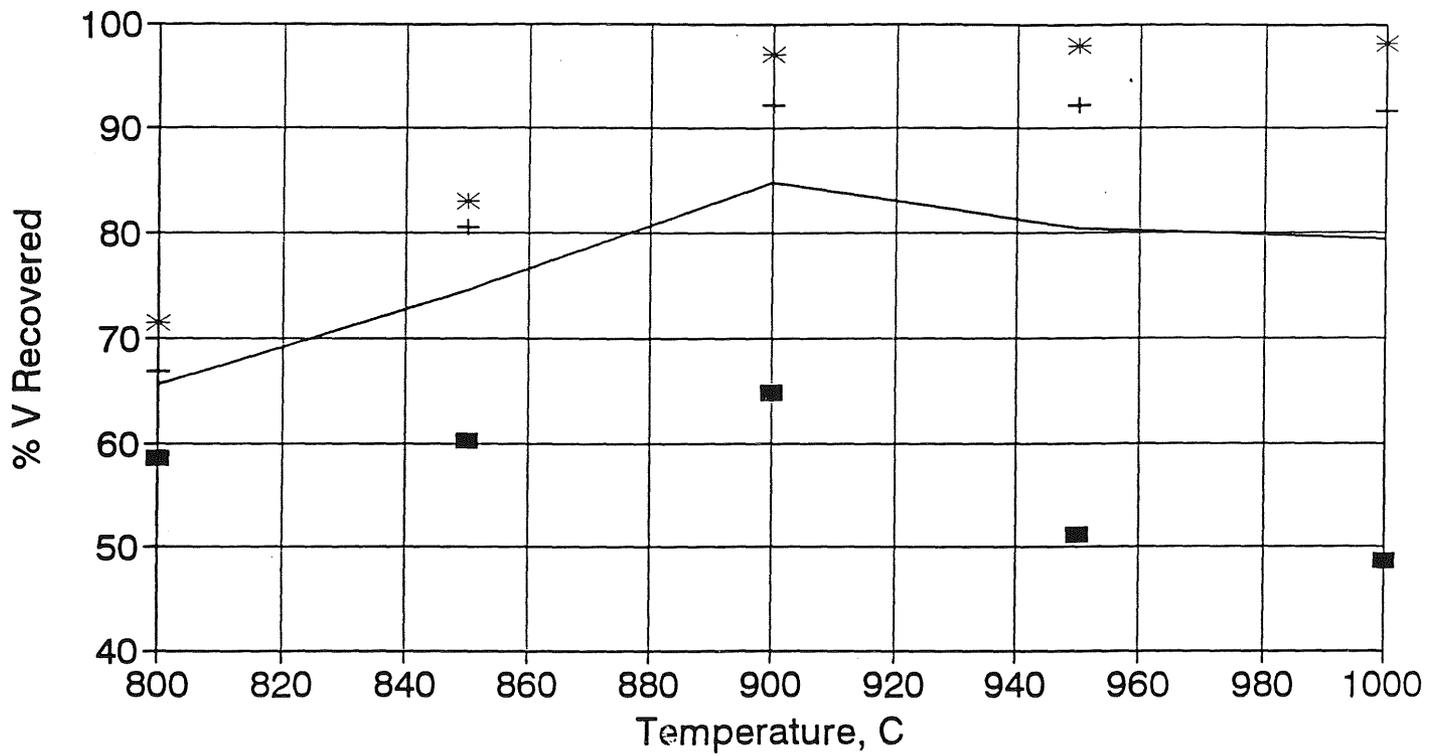


■ 9.1% NaCl + 23.1% NaCl * 37.5% NaCl — Average

Figure 16

Sodium Carbonate Roast Results

Recovery Based on V in Roasted Sample

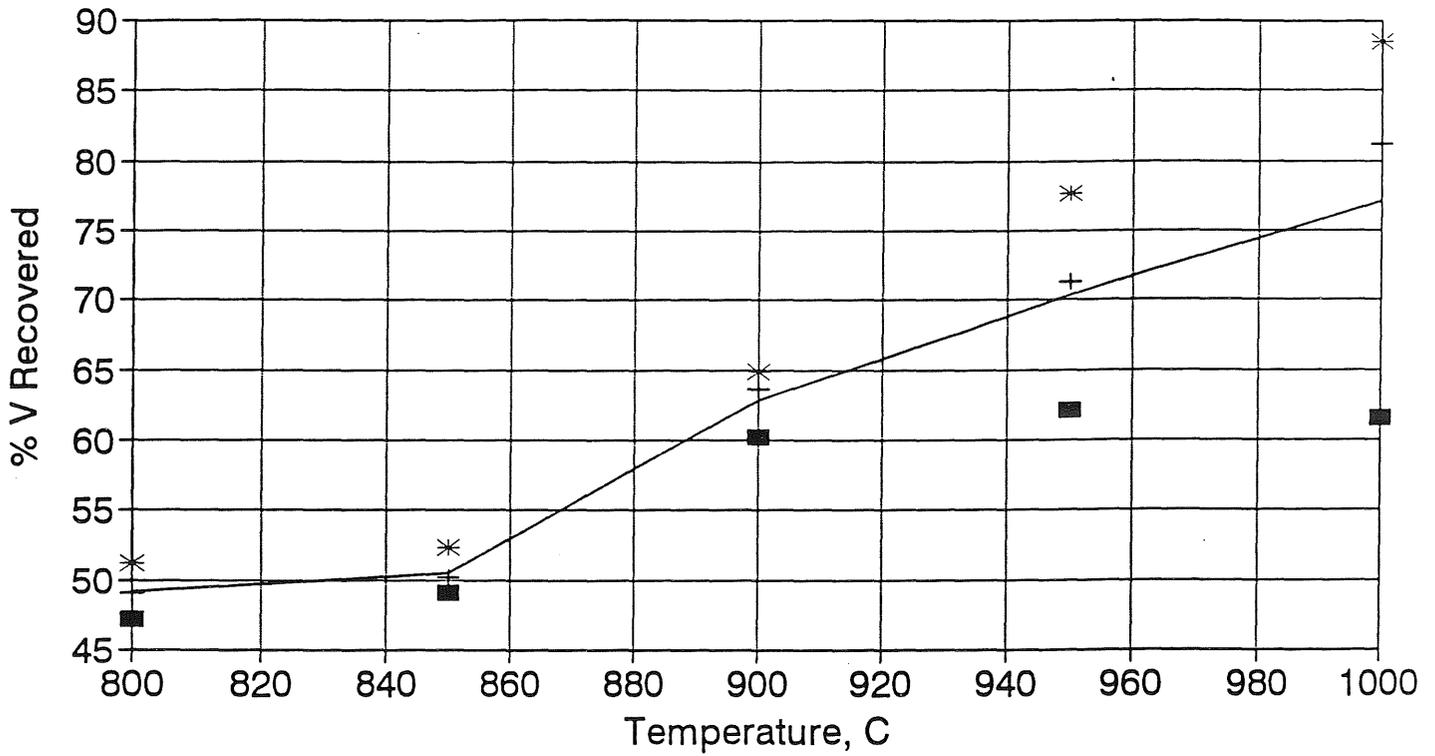


■ 9.1% Salt + 16.7% Salt * 23.1% Salt — Average

Figure 17

Sodium Sulfate Roast Results

Recovery Based on V in Roasted Sample



■ 9.1% Salt + 16.7% Salt * 23.1% Salt — Average

Figure 18

Vanadium Recovery from Ball Mill Feed

5 Mag. Separations on Mill Discharge

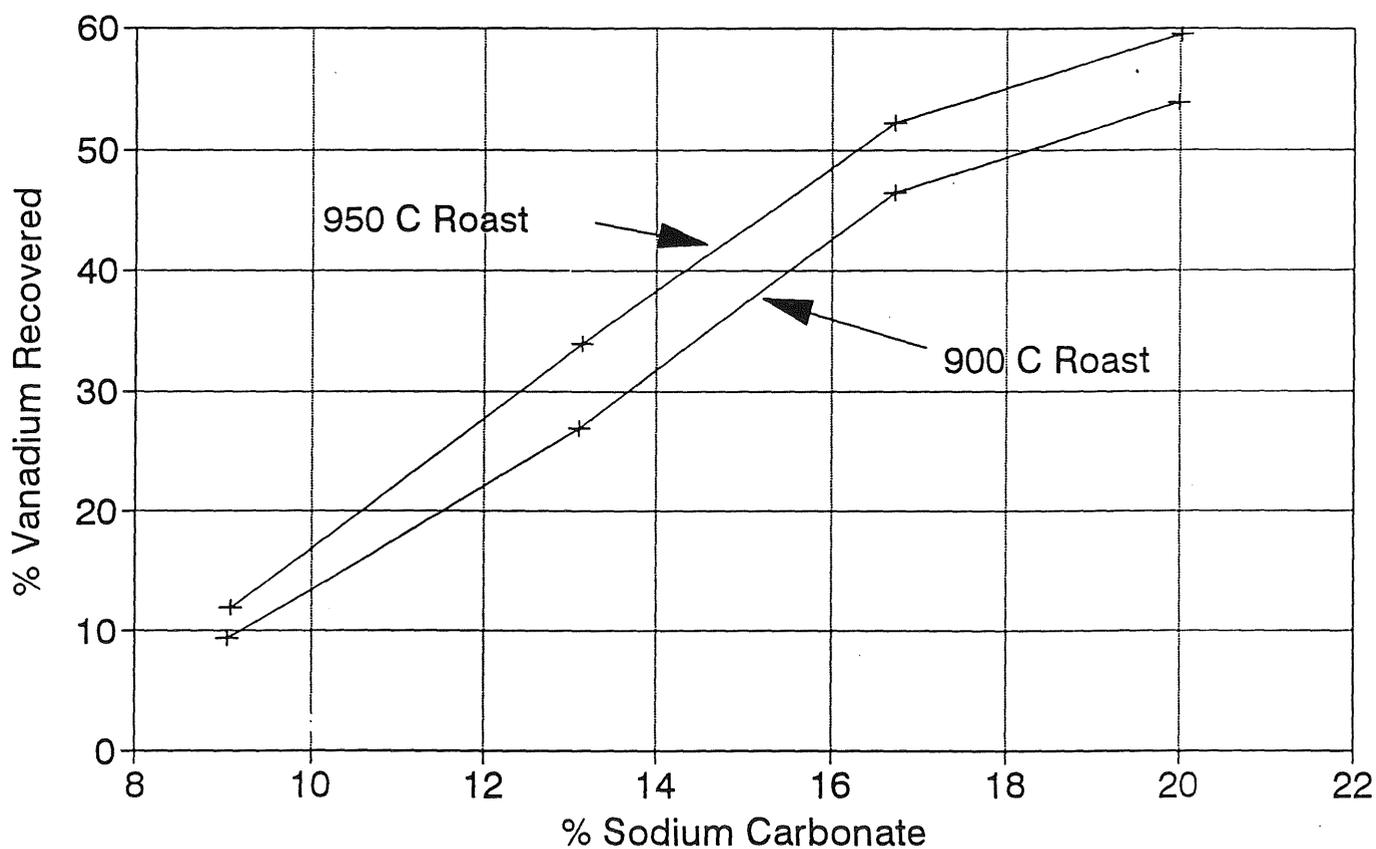


Figure 19

Sodium Carbonate Roasts of DT Conc.

Davis Tube on 25 Minute Ball Mill Grind

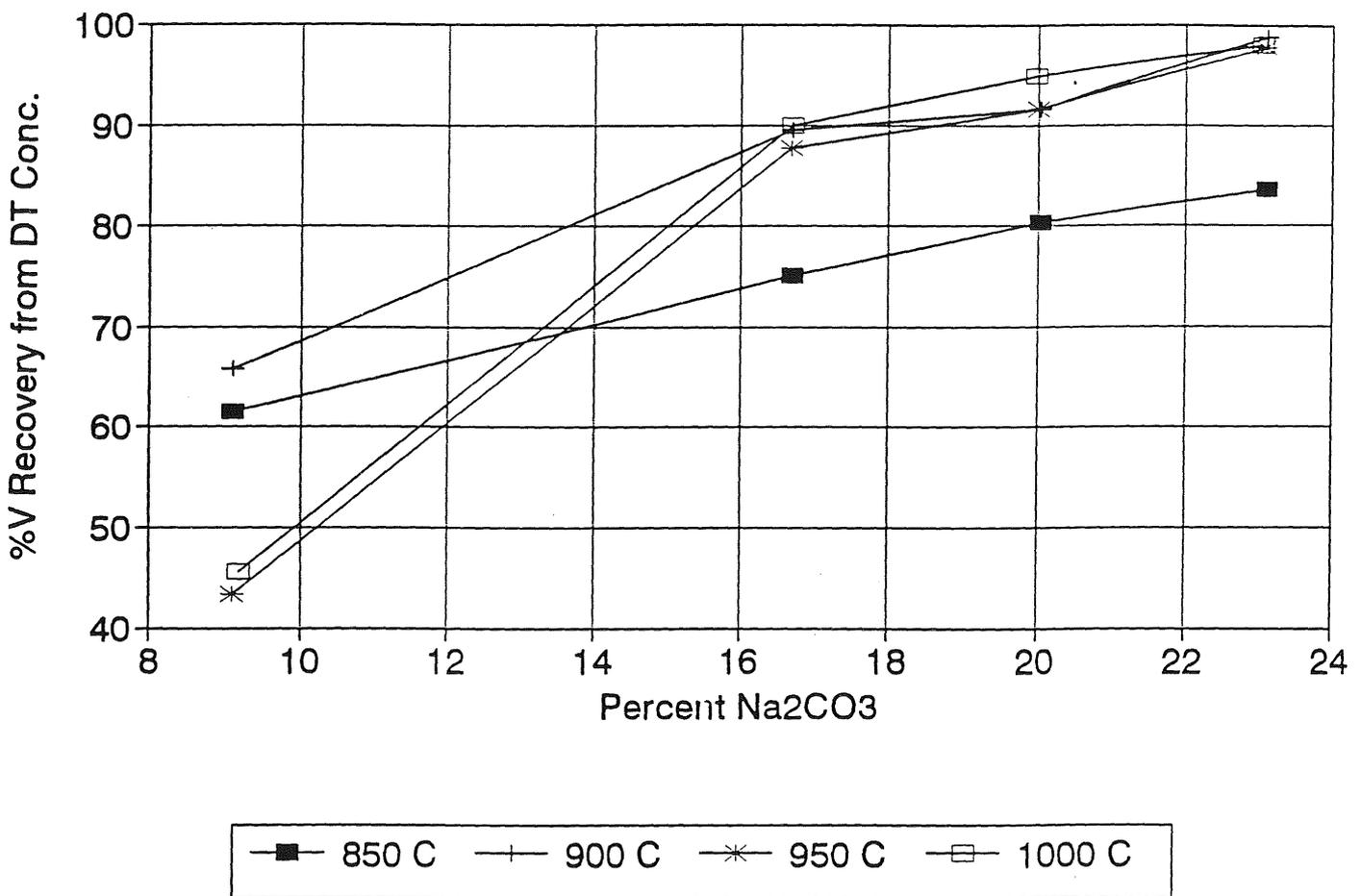


Figure 20

Sodium Carbonate Roasts of DT Conc.

Davis Tube on 25 Minute Ball Mill Grind

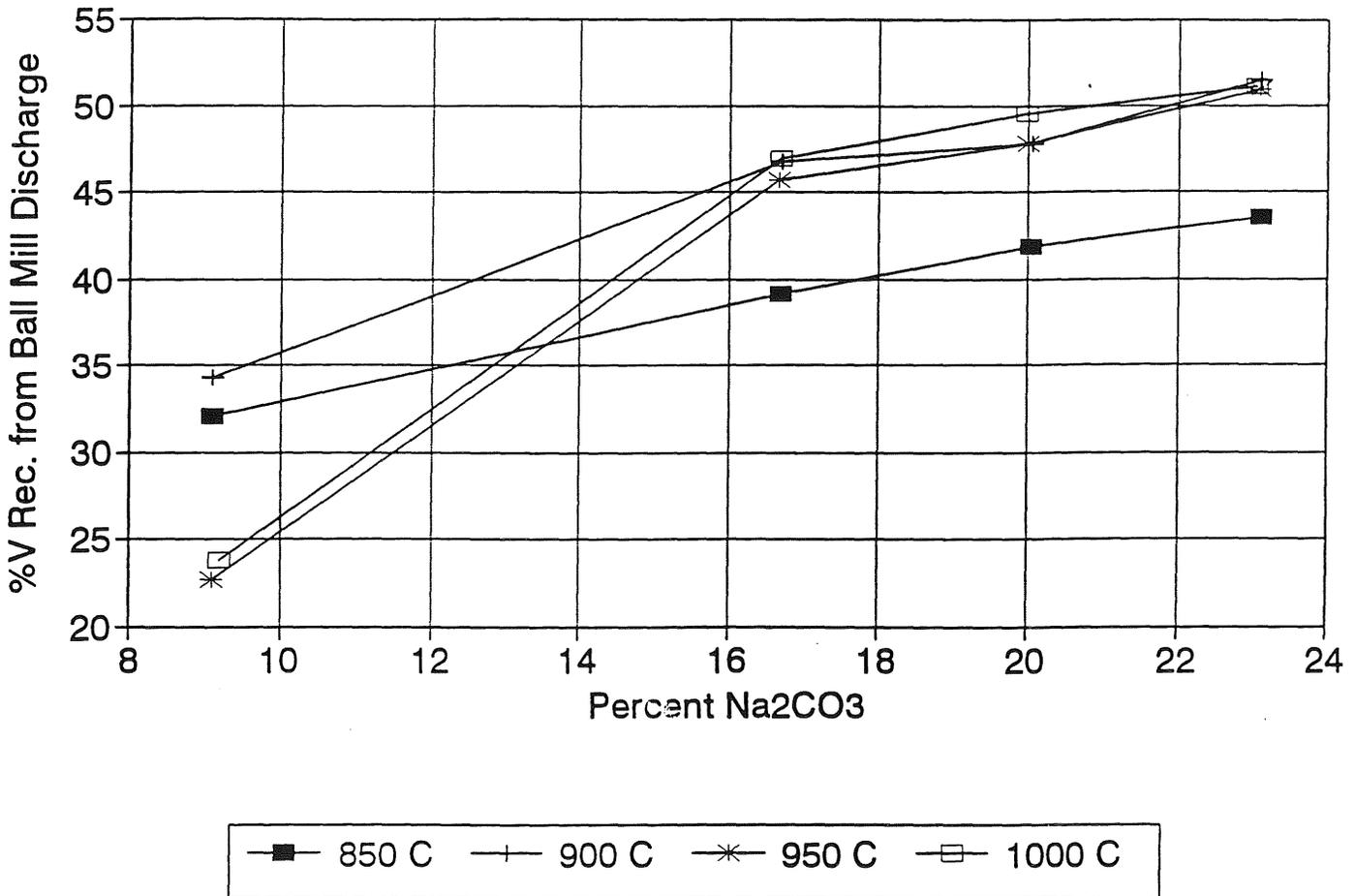
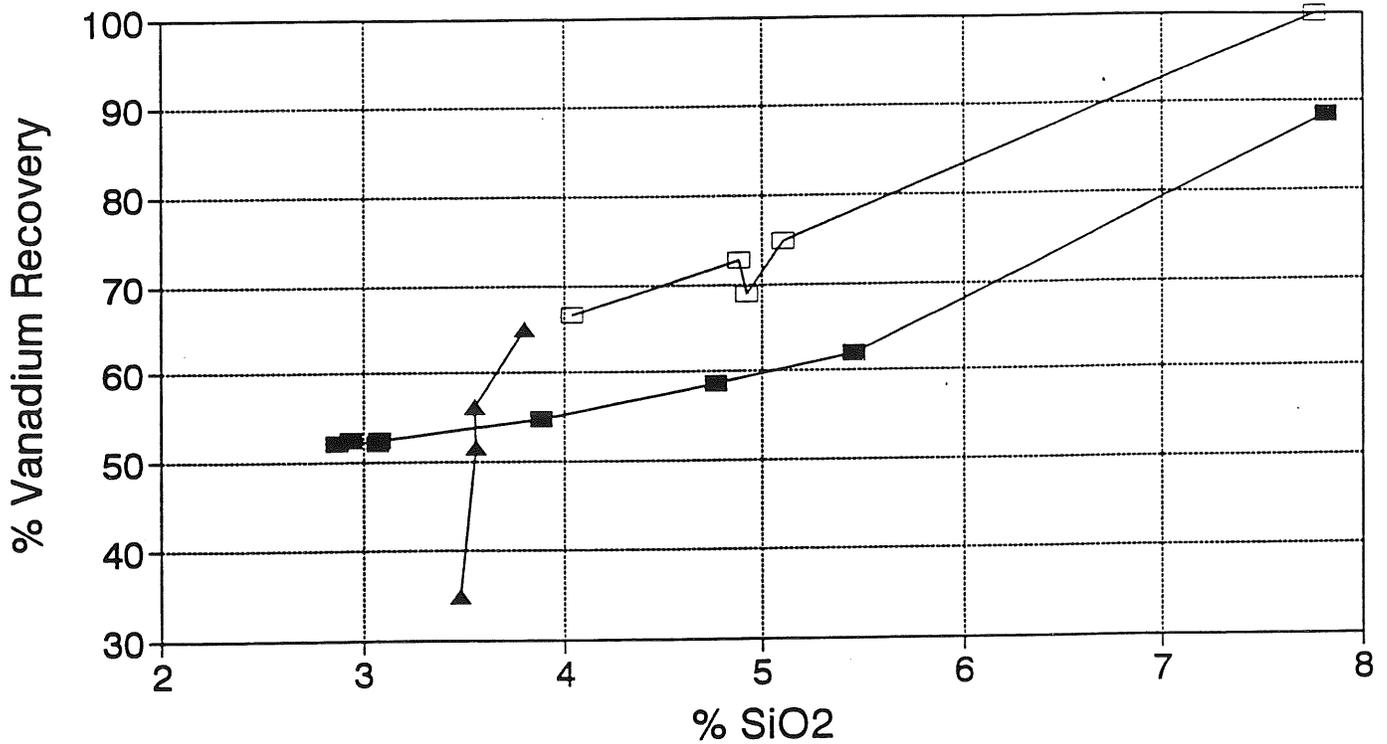


Figure 21

Vanadium Recovery - Physical Separation

Davis Tube, Magnetic Sep., Flotation

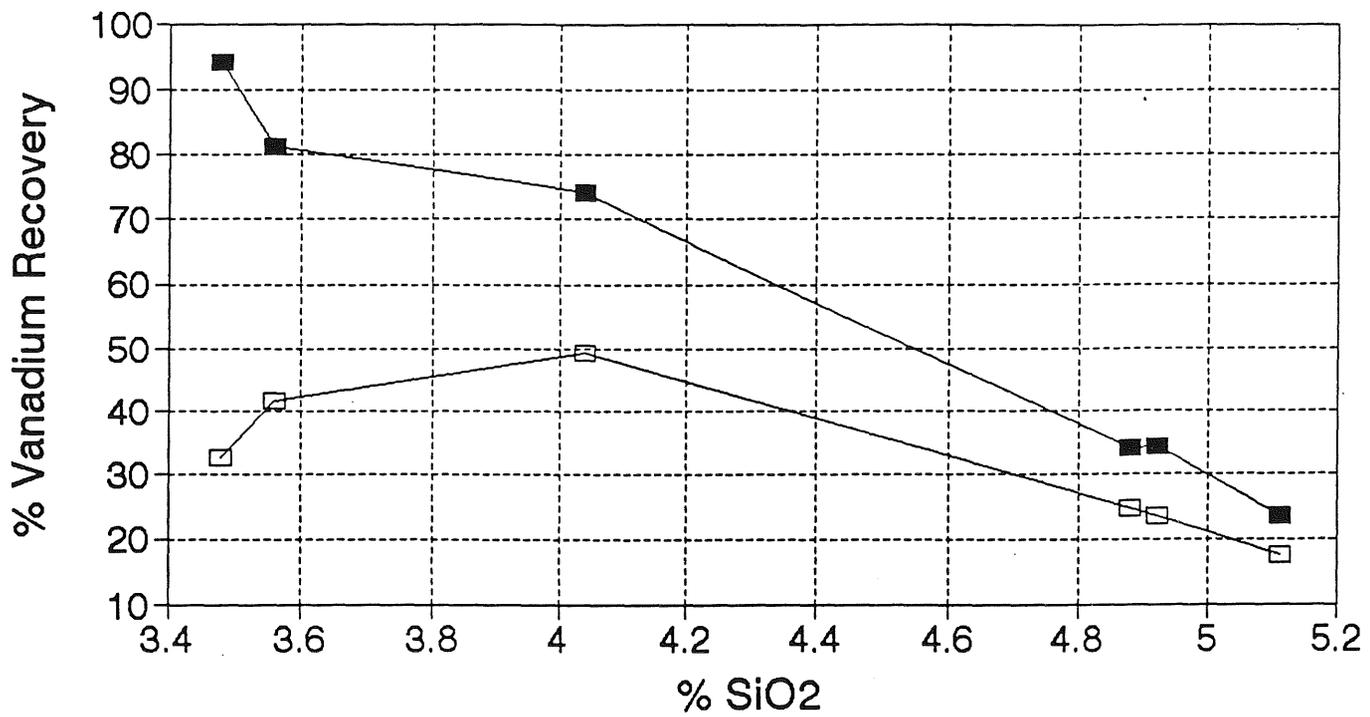


—■— Davis Tube Conc. —□— Mag.Sep. Conc. —▲— Flotation Conc.

Figure 22

Leach Recovery of Vanadium from Roast

Leach Recovery and Total Recovery



Data from Magnetic Separators and Flotation Concentrates

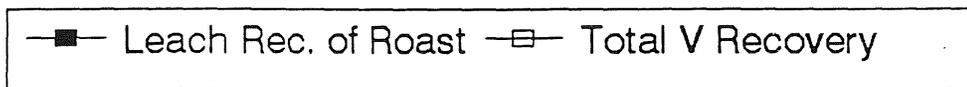


Figure 23

Roast Temperature vs Vanadium Recovery

Salt- 16% Na₂CO₃ - Flot. 0.222 lb Amine

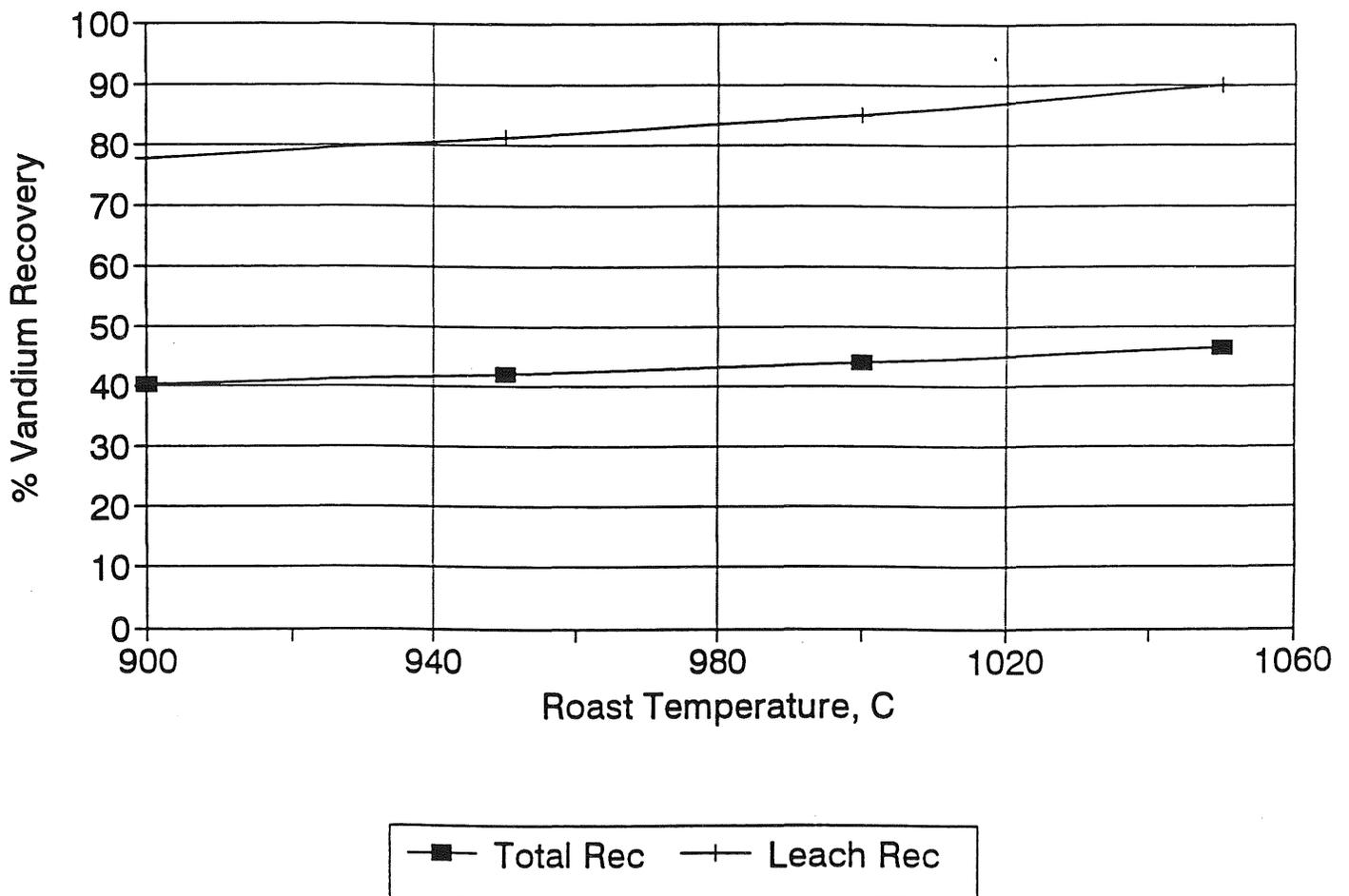


Figure 24

Roast Temperature vs Vanadium Recovery

Salt- 16% Na₂CO₃ - Flot. 0.444 lb Amine

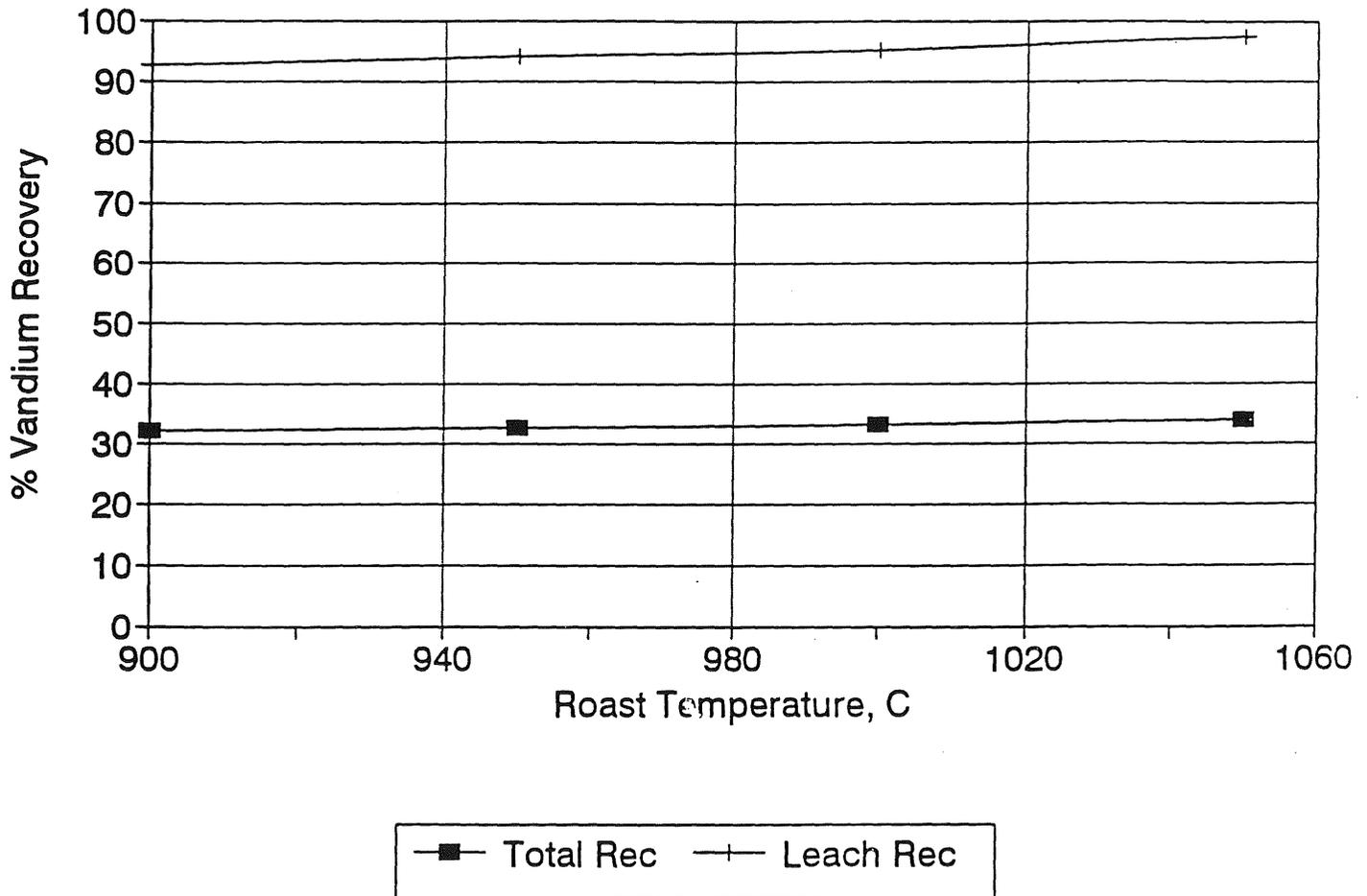
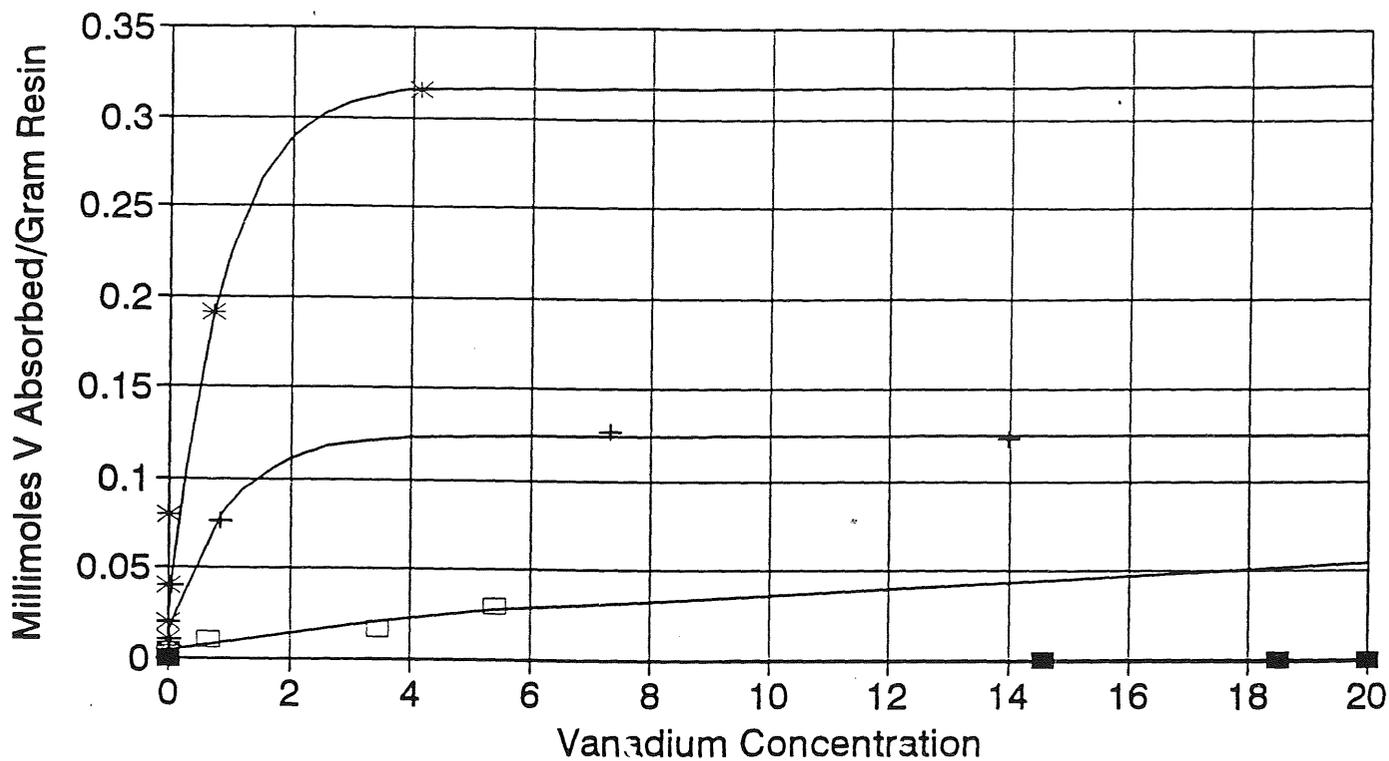


Figure 25

Ion Exchange Capacities of Resins

Determined Using 20.2 ppm V Solution



—■— Amberlite + Dow 1 * Dow 2 □ Diaion

Figure 26

Ion-Exchange Capacity vs pH

100 ml of Solution with 2 grams Resin

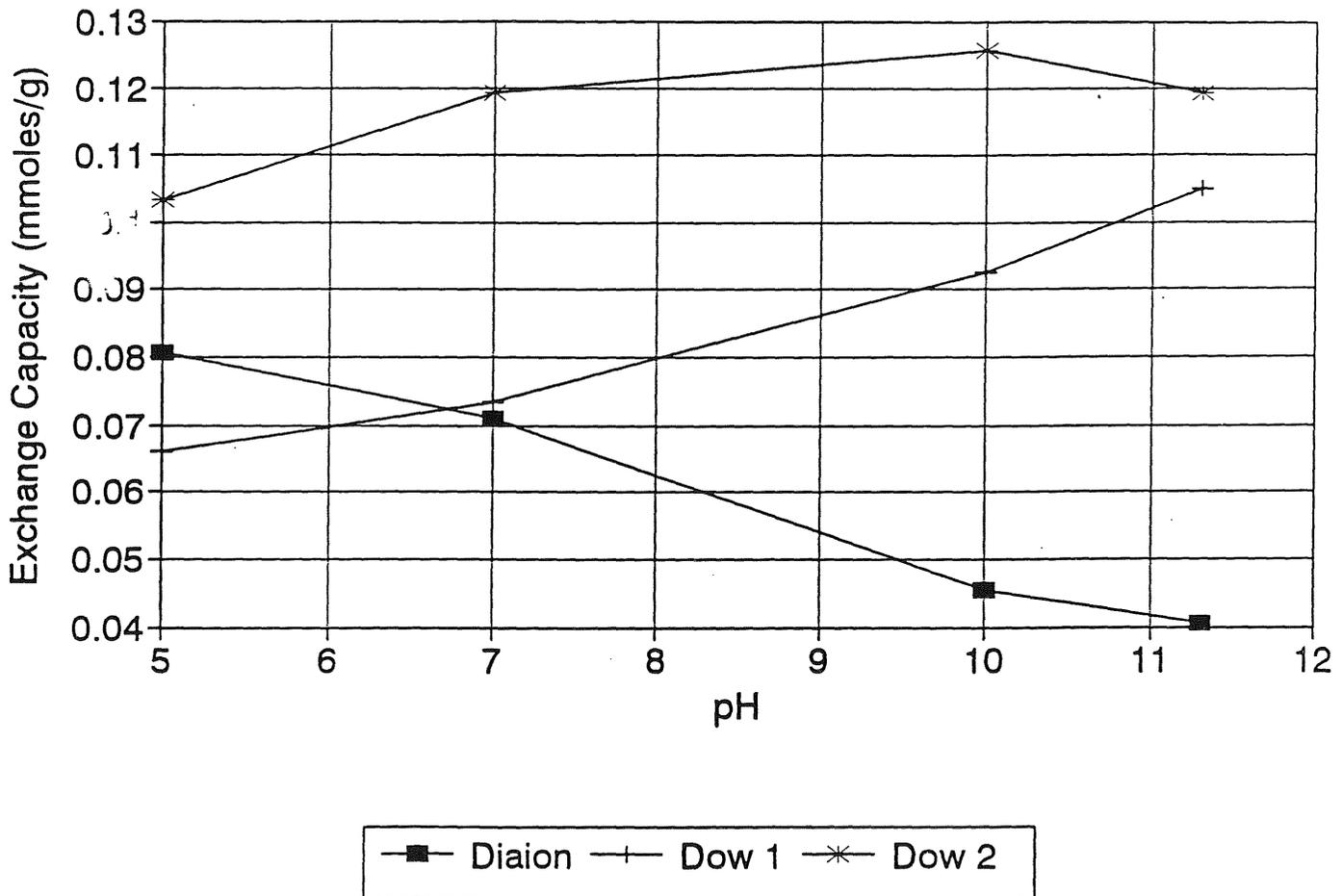
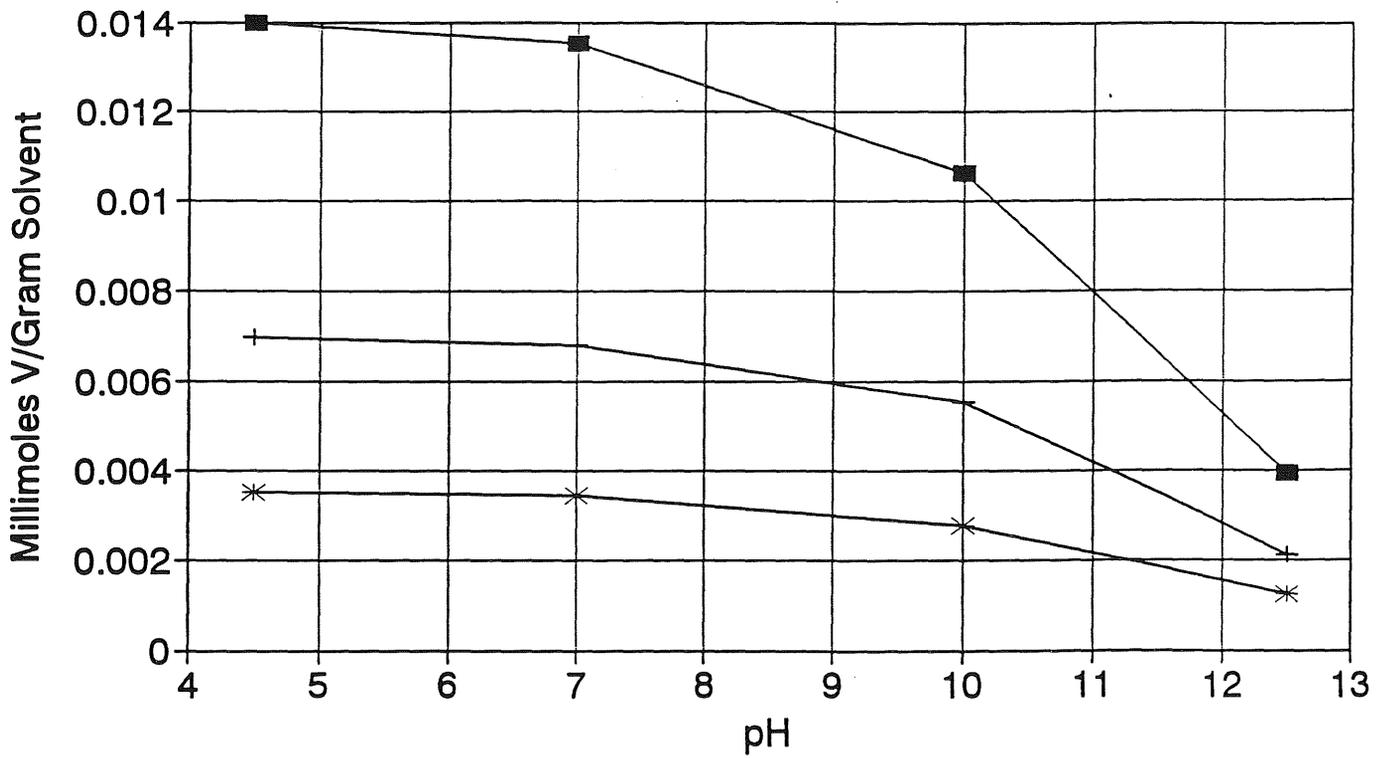


Figure 27

Solvent Extraction of Vanadium vs pH

Solvent - Aliquat 336

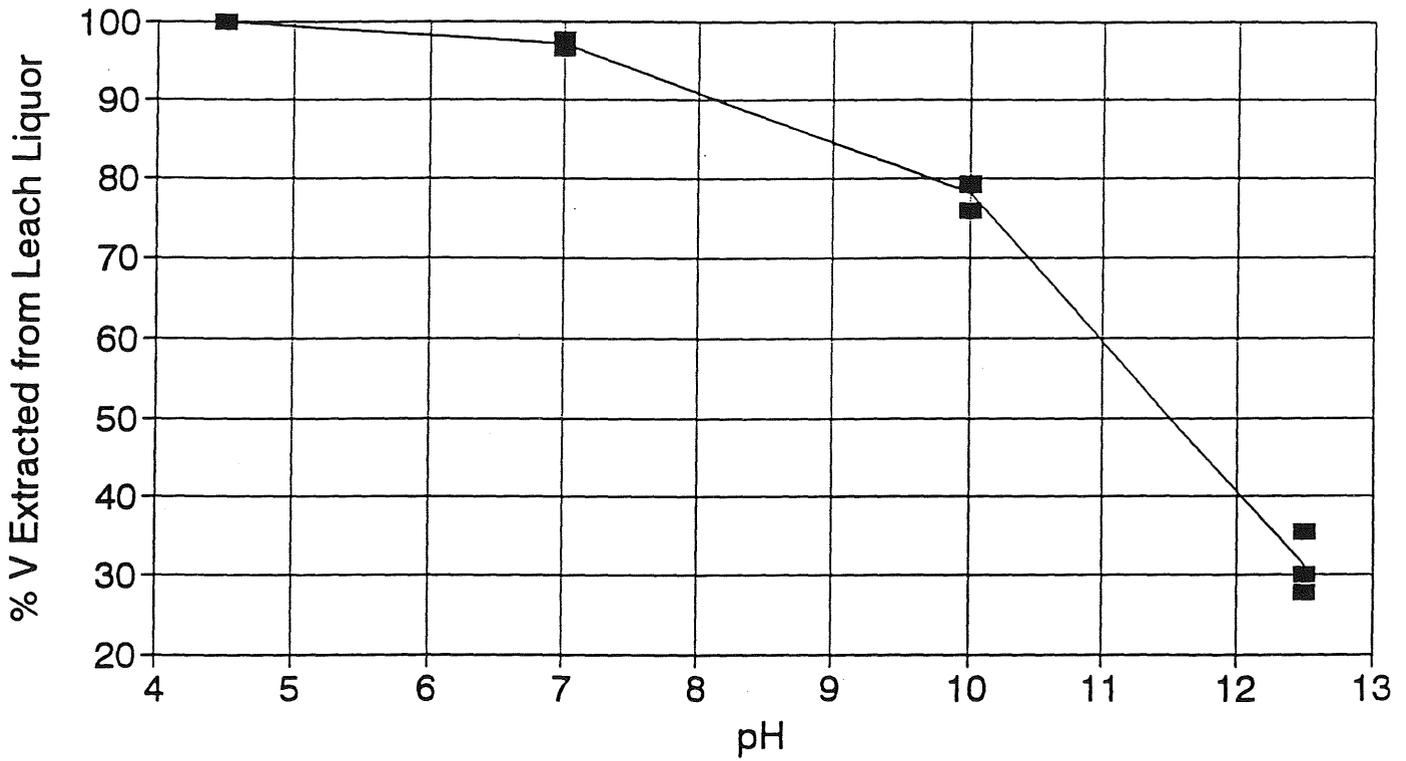


—■— 1:10 Solvent Ratio —+— 1:5 Solvent Ratio —*— 2:5 Solvent Ratio

Figure 28

Solvent Extraction of Vanadium vs pH

Solvent - Aliquat 336



■ Data Points — Average

Figure 29

Process Flow Scheme for Vanadiferous-Titaniferous Magnetite Ore

Rod Mill Grinding

Spiral Classifier

Magnetic Cobber

Magnetic Material to Ball Mill Grinding

Magnetic Separation

Magnetic Material to Amine Flotation

Flotation Underflow to Filtration

Balling with 15% Sodium Carbonate as the Binder

Fire the Balls in a Kiln or Straight Grate a 1000 C

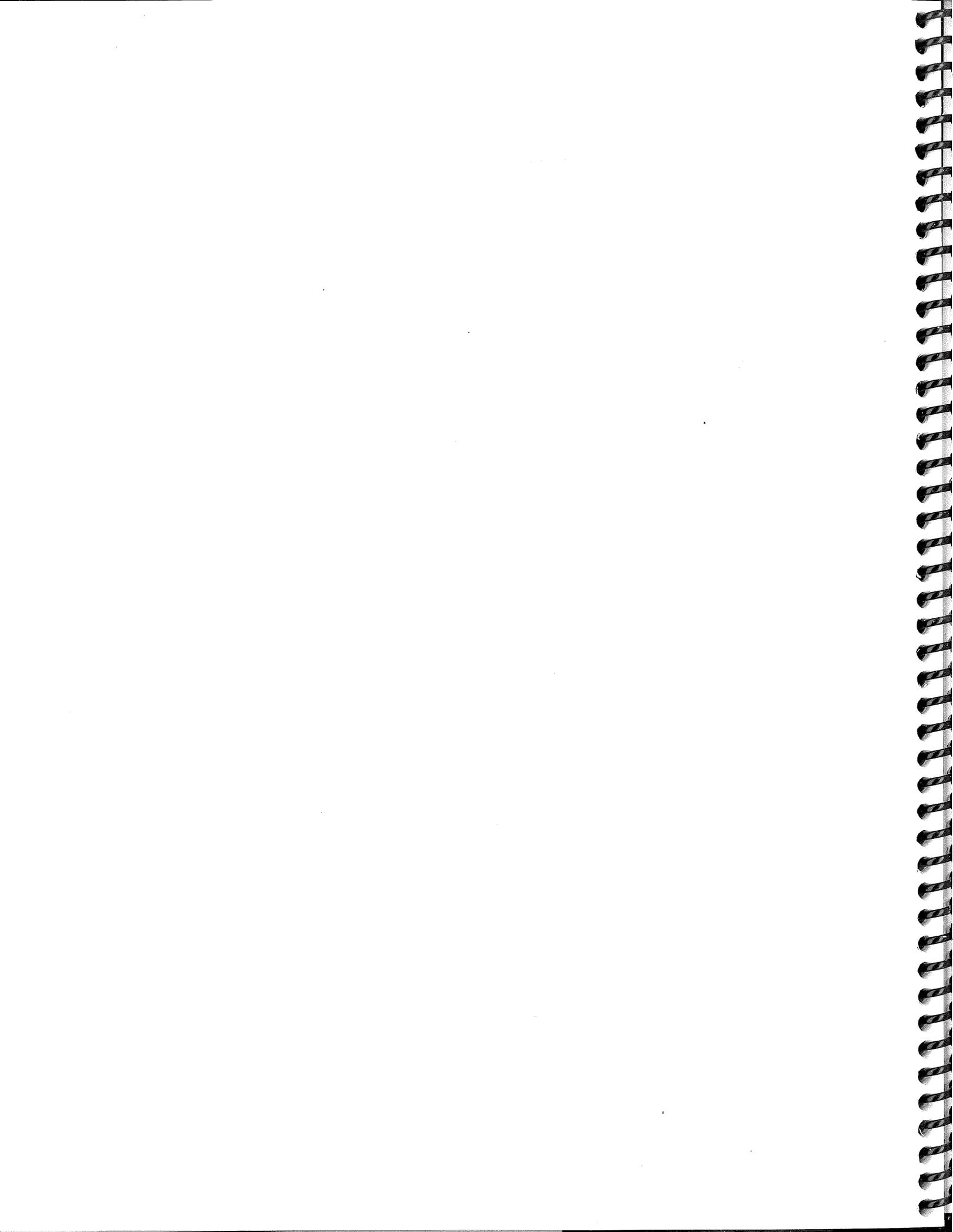
Leach the Fired Pellets in Water at 80 C

Precipitate the Vanadium as "Red Cake" at pH 2.5

Filter the Precipitate

Ion-Exchange or Solvent Extraction of V from the Filtrate

Strip and Precipitate Vanadium from the Resin or Solvent



Appendix 1

Liberation Grind Tests

Mill and Ball Charge

The ball mill is 6 inches in diameter and 4 inches long on the inside and runs at 100 rpm when empty or 96 rpm with charge. The balls are made by the Sheffield Division of Armco Steel Corporation. Composition of the ball charge is given below:

| <u>Ball Size,</u> <u>inches</u> | <u>No. of</u> <u>Balls</u> | <u>Weight,</u> <u>grams</u> |
|------------------------------------|-------------------------------|--------------------------------|
| 1/2 | 117 | 1160 |
| 3/4 | <u>77</u> | <u>2450</u> |
| | 194 | 3610 |

The total weight of a new ball charge may range from 3590 to 3630 grams. The ball charge should be weighed periodically and the weights of the 1/2-inch and 3/4-inch portions recorded.

Test Procedure

1. The Magnetic cobber concentrate from the ilmenite grinding circuit is used as the feed material for the following liberation grinds.
2. Mix and split out about 2 kilograms.
3. Roll and mix thoroughly and riffle out about 825 grams.
4. Riffle in quarters and adjust each sample to exactly 200 grams.
5. Use 200 grams minus 20-mesh material and 100-ml H₂O (66.7% solids).
6. Four grinding tests will be run using times of 6, 9, 12, and 17 minutes.
7. When a 200-gram sample has been ground the desired time, the mill is dumped into a metal hopper with a coarse screen to hold the grinding balls. The mill, cover, and balls are washed clean and sample transferred to a beaker, and demagnetized,
8. The demagnetized sample is then run through standard screening procedures to determine the amount of sample that passes through a 270 mesh screen.
9. The 6-minute grind is run first.

10. With the grinds completed, a standard Davis-tube test is done on each grind and the concentrates are sent in for chemical analysis.
11. Recombine the plus and minus 270-mesh material and mix thoroughly prior to Davis-tube separation.

The Davis-tube procedure is as follows:

| | |
|--------------------------------------|-----------------------------|
| Sample Weight | - 10 grams |
| Operating Time | - 15 minutes |
| Water Rate | - 0.4 gpm |
| Tube Speed | - 90-100 strokes per minute |
| Field Current and Strength at Gap | - 1.6 amps (5000 gauss) |

Record percent weight recovery and analyze concentrate for Fe, SiO₂ and V₂O₅.

Appendix 2

Batch Ball Mill Grinding Tests.

Follow the follow grinding procedure for the 22.0 minute, 23.5 minute and 25.0 minute grinds.

Weigh out the following ball charge into the 12 inch mill.

30 pounds of 3/4 inch balls

14.5 pounds of 1/2 inch balls

Weigh and record the weight of the balls before each grind to ensure none were lost in the previous grind.

Ensure that the mill turns at 70 rpm. Add 2000 grams of dried sample to the mill with 1000 grams of water. Set the timer on the mill to the required grind time and turn the mill on. The timer will automatically shut the mill off when the clock is at zero.

When the grind is complete, empty the mill through the mill trommel and into a large pan. The trommel will screen out the grinding balls. Ensure that no balls enter the sample. Thoroughly rinse the balls off and rinse the mill out. Filter the ground sample and store the filter cake in a covered container so that it won't dry out.

Appendix 3

Vanadium Flotation

All flotation tests are run using 3.5 ml of 1% Methyl Isobutyl Carbinol as the frother. The amine flotation reagent is a 10,000 mg/liter solution of Sherex MG 83 Amine in distilled water. The flotation tests are performed using 1000 grams of concentrate on a dry basis and then floated at 35% solids.

Flotation Test 1. - 0.089 lb/LTon - Add 4 ml of the Amine solution and 3.5 ml of MIBC. Collect the froth for 0.5, 1.0, 1.5, 2.0 and 3.0 minutes. Filter each froth sample and the concentrate underflow and submit all 6 samples to the Chem Lab for V2O5 and SiO2 analyses.

Flotation Test 2. - 0.156 lb/LTon - Add 7 ml of the Amine solution and 3.5 ml of MIBC. Collect the froth for 0.5, 1.0, 1.5, 2.0 and 3.0 minutes. Filter each froth sample and the concentrate underflow and submit all 6 samples to the Chem Lab for V2O5 and SiO2 analyses.

Flotation Test 3. - 0.222 lb/LTon - Add 10 ml of the Amine solution and 3.5 ml of MIBC. Collect the froth for 0.5, 1.0, 1.5, 2.0 and 3.0 minutes. Filter each froth sample and the concentrate underflow and submit all 6 samples to the Chem Lab for V2O5 and SiO2 analyses.

Flotation Test 4. - 0.444 lb/LTon - Add 20 ml of the Amine solution and 3.5 ml of MIBC. Collect the froth for 0.5, 1.0, 1.5, 2.0 and 3.0 minutes. Filter each froth sample and the concentrate underflow and submit all 6 samples to the Chem Lab for V2O5 and SiO2 analyses.

Appendix 4

Salt Roasting Test Procedures

Initial Salt Roasting Tests

The weight of the sample and the weight of the roasting salt should be recorded to 4 decimal places for each test.

The following tests will be performed with the Davis Tube concentrate from the sample that was pulverized to 100 percent passing 200 mesh.

SODIUM CHLORIDE ROASTS.

Test 1 to 5. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.10 grams of sodium chloride with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 6 to 10. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.30 grams of sodium chloride with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 11 to 15. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.60 grams of sodium chloride with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach

solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

SODIUM SULFATE ROASTS.

Test 16 to 20. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.10 grams of sodium sulfate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 21 to 25. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.20 grams of sodium sulfate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 26 to 30. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.30 grams of sodium sulfate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

SODIUM CARBONATE ROASTS.

Test 31 to 35. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.10 grams of sodium carbonate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When

the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 36 to 40. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.20 grams of sodium carbonate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

Test 41 to 45. Weigh FIVE 1.00 gram samples into 5 separate platinum crucibles and mix in 0.30 grams of sodium carbonate with each sample. Roast one sample at each of the following temperatures for 100 minutes: 800 C, 850 C, 900 C, 950 C, and 1000 C. Remove the sample from the muffle and allow it to cool. When the sample and crucible are cool, place the crucible and sample into a 250 ml beaker and add 200 ml of distilled water. Cover the sample and place it on a magnetic-stirrer-hot plate. As the sample is stirring, heat it to 80 C and allow it to remain at that temperature for 2 hours with continued agitation. Remove the sample from the hot plate and filter 40 ml of the leach solution through a GF-A Whatman glass filter paper. Submit the filtered leach solution for ICP analysis.

SODIUM CARBONATE ROASTING TESTS

The weight of the sample and the weight of the sodium carbonate should be recorded to 4 decimal places for each test.

The following tests will be performed with the samples that were obtained prior to the magnetic separation.

For tests 46 - 51, 1.00 gram of sample is mixed with 0.10 grams of sodium carbonate.

Test 46. Weigh the 22 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 47. Weigh the 22 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Test 48. Weigh the 23.5 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 49. Weigh the 23.5 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Test 50. Weigh the 25 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 51. Weigh the 25 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Tests 52 to 57. For tests 52-57, repeat each of the above tests using 0.20 grams of sodium carbonate.

After each sample has been roasted, allow it to cool for about 30 minutes. Rinse the crucible and contents into a tared 250 ml beaker. Bring the sample to 200 ml by weight with DI water. Place the sample on a stirring hot plate and as the solution is stirring heat it to 80 C. Stir and heat the solution for 2 hours. Filter at least 40 ml of the solution using Whatman GA-A glass filter paper, and submit the solution for ICP analyses.

The following tests will be performed with the samples that were obtained after one pass through the drum-magnetic separator.

For tests 58 - 63, 1.00 gram of sample is mixed with 0.10 grams of sodium carbonate.

Test 58. Weigh the 22 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 59. Weigh the 22 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Test 60. Weigh the 23.5 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 61. Weigh the 23.5 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Test 62. Weigh the 25 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 900 C.

Test 63. Weigh the 25 minute grind into a platinum crucible and mix in the sodium carbonate. Roast for 100 minutes at 950 C.

Tests 64 to 69. For tests 64-69, repeat each of the above tests using 0.20 grams of sodium carbonate.

After each sample has been roasted, allow it to cool for about 30 minutes. Rinse the crucible and contents into a tared 250 ml beaker. Bring the sample to 200 ml by weight with DI water. Place

the sample on a stirring hot plate and as the solution is stirring heat it to 80 C. Stir and heat the solution for 2 hours. Filter at least 40 ml of the solution using Whatman GA-A glass filter paper, and submit the solution for ICP analyses.

The following tests will be performed with the 25 minute grind sample that was obtained after five passes through the drum-magnetic separator.

Test 70 - 71. Weigh two 1.00 gram of the samples and mix with 0.10 grams of sodium carbonate and roast one at 900 C and one at 950 C.

Test 72 - 73. Weigh two 1.00 gram of the samples and mix with 0.15 grams of sodium carbonate and roast one at 900 C and one at 950 C.

Tests 74 - 75. Weigh two 1.00 gram samples and mix them with 0.20 grams of sodium carbonate. Roast one sample at 900 C and one at 950 C.

Tests 76 - 77. Weigh two 1.00 gram samples and mix them with 0.25 grams of sodium carbonate. Roast one sample at 900 C and one at 950 C.

After each sample has been roasted, allow it to cool for about 30 minutes. Rinse the crucible and contents into a tared 250 ml beaker. Bring the sample to 200 ml by weight with DI water. Place the sample on a stirring hot plate and as the solution is stirring heat it to 80 C. Stir and heat the solution for 2 hours. Filter at least 40 ml of the solution using Whatman GA-A glass filter paper, and submit the solution for ICP analyses.

25 Minute Grind Davis Tube Roasts.

Tests 78 - 81. Use the DT Conc. of the 25 minute grind for these 4 tests. Weigh four 1 gram samples into 4 crucibles. Add 0.1, 0.2, 0.25, and 0.3 grams of sodium carbonate to the 4 crucibles respectively. Roast the 4 samples at 850 C.

Tests 82 - 85. Use the DT Conc. of the 25 minute grind for these 4 tests. Weigh four 1 gram samples into 4 crucibles. Add 0.1, 0.2, 0.25, and 0.3 grams of sodium carbonate to the 4 crucibles respectively. Roast the 4 samples at 900 C.

Tests 86 - 89. Use the DT Conc. of the 25 minute grind for these 4 tests. Weigh four 1 gram samples into 4 crucibles. Add 0.1, 0.2, 0.25, and 0.3 grams of sodium carbonate to the 4 crucibles respectively. Roast the 4 samples at 950 C.

Tests 90 - 93. Use the DT Conc. of the 25 minute grind for these 4 tests. Weigh four 1 gram samples into 4 crucibles. Add 0.1, 0.2, 0.25, and 0.3 grams of sodium carbonate to the 4 crucibles respectively. Roast the 4 samples at 1000 C.

After each sample has been roasted, allow it to cool for about 30

minutes. Rinse the crucible and contents into a tared 250 ml beaker. Bring the sample to 200 ml by weight with DI water. Place the sample on a stirring hot plate and as the solution is stirring heat it to 80 C. Stir and heat the solution for 2 hours. Filter at least 40 ml of the solution using Whatman GA-A glass filter paper, and submit the solution for ICP analyses.

Flotation Roasting Tests

The following tests use the flotation concentrate underflow from the flotation tests that were run with the 25 minute ball grind material that was passed through the drum separator 5 times.

Test 94 -95. Use the Flotation Conc. (4ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 900 C.

Test 96 -97. Use the Flotation Conc. (4ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 950 C.

Test 98 -99. Use the Flotation Conc. (7ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 900 C.

Test 100 -101. Use the Flotation Conc. (7ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 950 C.

Test 102 -103. Use the Flotation Conc. (10ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 900 C.

Test 104 -105. Use the Flotation Conc. (10ml Amine) for these 2 tests. Weigh 2 1 gram samples into 2 crucibles. Add 0.1 and 0.15 grams of sodium carbonate to the 2 crucibles. Roast the samples at 950 C.

Test 106 -108. Use the Flotation Conc. (20ml Amine) for these 3 tests. Weigh 3 1 gram samples into 3 crucibles. Add 0.1, 0.15 and 0.20 grams of sodium carbonate to the 3 crucibles. Roast the samples at 900 C.

Test 109 -111. Use the Flotation Conc. (20ml Amine) for these 3 tests. Weigh 3 1 gram samples into 3 crucibles. Add 0.1, 0.15 and 0.20 grams of sodium carbonate to the 3 crucibles. Roast the samples at 950 C.

After each sample has been roasted, allow it to cool for about 30 minutes. Rinse the crucible and contents into a tared 250 ml beaker. Bring the sample to 200 ml by weight with DI water. Place the sample on a stirring hot plate and as the solution is stirring heat it to 80 C. Stir and heat the solution for 2 hours. Filter at least 40 ml of the solution using Whatman GA-A glass filter paper, and submit the solution for ICP analyses.

Appendix 5

Ion-Exchange Resins

The following four ion-exchange resins are to be used in the ion-exchange tests.

1. Amberlite - Strongly acidic cation exchange resin. Active group is Sulfonic acid.
2. Dowex 1 - Strongly basic anion exchange resin. Active group is Trimethylbenzylammonium. Capacity 0.7 meq/ml.
3. Dowex 2 - Strongly basic anion exchange resin. Active group is Dimethylethanolbenzylammonium. Capacity 1.2 meq/ml
4. Diaion WA30 - Weakly basic anion exchange resin. Active group is Alkylamine. Ionic form is free base. Capacity 1.5 meq/ml.

Initial Ion Exchange Tests

The initial ion exchange tests are run with the vanadate solutions that were saved from the sodium carbonate roasting tests of the flotation concentrate samples. Measure the pH of the solution and neutralize it to pH 7 using sulfuric acid. Filter the neutralized solution through a GA-A glass filter to eliminate any solids that are present. Submit the solution for analysis of V, Na, and Si.

Tests 1 - 4. Weigh 10 grams of each ion-exchange resin (Amberlite, Diaion WA30, Dow 1, and Dow 2) into 4 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 5 - 8. Weigh 5 grams of each ion-exchange resin (Amberlite, Diaion WA30, Dow 1, and Dow 2) into 4 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 9 - 11. Weigh 2 grams of each anion-exchange resin (Diaion WA30, Dow 1, and Dow 2) into 3 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 12 - 14. Weigh 2 grams of each anion-exchange resin (Diaion WA30, Dow 1, and Dow 2) into 3 separate 250 ml Erlenmeyer flasks. To each flask, add 100 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 15 - 17. Weigh 0.5 grams of each anion-exchange resin (Diaion WA30, Dow 1, and Dow 2) into 3 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 18 - 19. Weigh 0.5 grams of each of the 2 Dow anion-exchange resins (Dow 1, and Dow 2) into 2 separate 250 ml Erlenmeyer flasks. To each flask, add 100 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 20 - 21. Weigh 0.1 grams of each of the 2 Dow anion-exchange resins (Dow 1, and Dow 2) into 2 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Tests 22 - 23. Weigh 0.05 grams of each of the 2 Dow anion-exchange resins (Dow 1, and Dow 2) into 2 separate 250 ml Erlenmeyer flasks. To each flask, add 50 ml of the pH 7 vanadate solution. Place a rubber stopper in the top of each flask and shake each flask and contents for 2 minutes. Remove the stoppers and filter the samples through a GA-A glass filter. Submit the filtered solutions for analysis of V, Na, and Si.

Ion -Exchange Capacity for Precipitate Filtrate

The following procedure involves using the vanadium red cake solution.

1. Weigh 1.00 grams of Diaion WA30 ion exchange resin into a clean 250 ml Erlenmeyer flask. Using a graduated cylinder, add 25 ml of the red cake solution and shake for 5 minutes. Allow the solution to stand for 15 minutes. Filter the solution through a Whatman GF-A glass filter paper into a small sample bottle. Submit the filtered solution to the Chem Lab for analysis.

2. Weigh 0.50 grams of Dow 1 ion exchange resin into a clean 250 ml Erlenmeyer flask. Using a graduated cylinder, add 38 ml of the red cake solution and shake for 5 minutes. Allow the solution to stand for 15 minutes. Filter the solution through a Whatman GF-A glass filter paper into a small sample bottle. Submit the filtered solution to the Chem Lab for analysis.

3. Weigh 0.20 grams of Dow 2 ion exchange resin into a clean 250 ml Erlenmeyer flask. Using a graduated cylinder, add 50 ml of the red cake solution and shake for 5 minutes. Allow the solution to stand for 15 minutes. Filter the solution through a Whatman GF-A glass filter paper into a small sample bottle. Submit the filtered solution to the Chem Lab for analysis.

Ion-Exchange pH Tests

The following procedure involves using the Vanadium Leach Solution.

The original 1400 ppm Vanadium Leach Solution is diluted by 1 in 10 to make a 140 ppm Vanadium Leach Solution. This 140 ppm Vanadium Leach Solution will be used in the pH ion exchange tests.

I. Using a 250 ml graduated cylinder, measure 200 ml of the original 1400 ppm Vanadium Leach Solution into a 2 liter volumetric flask. Bring the volume in the flask to the mark with RO water. Invert the flask several times to mix it well. This solution will be the 140 ppm Vanadium Leach Solution.

II. Measure the pH of the 140 ppm Vanadium Leach Solution and record it.

III. Pour approximately 400 ml of the 140 ppm V Leach Solution into a beaker and adjust the pH to 10.0 using 3 Molar Sulfuric Acid.

IV. Pour approximately 400 ml of the 140 ppm V Leach Solution into a beaker and adjust the pH to 7.0 using 3 Molar Sulfuric Acid.

V. Pour approximately 400 ml of the 140 ppm V Leach Solution into a beaker and adjust the pH to 5.0 using 3 Molar Sulfuric Acid.

Using the above 4 solutions - "as is" pH, 10.0 pH, 7.0 pH and 5.0 pH- perform the following procedure with the 3 ion exchange resins at each pH.

1. Label 3 clean 25 ml Erlenmeyer flasks as Dow 1, Dow 2, and Diaion WA30.

2. Weigh 2.00 grams of each ion exchange resin - Dow 1, Dow 2, and Diaion WA30 - into 3 clean 250 ml Erlenmeyer flask. Using a

100 ml graduated cylinder, add 100 ml of the Vanadium Leach Solution and shake for 5 minutes. Allow the solution to stand for 15 minutes. Filter the solution through a Whatman GF-A glass filter paper into a small sample bottle for ICP analysis.

3. Label the sample bottle with the appropriate pH and the appropriate name of the ion exchange resin.

Note: There will be 3 ion exchange resins at each of 4 pH. This will make a total of 12 tests.

Appendix 6

Solvent Extraction of Vanadium

An amine named Aliquat 336 is used to extract the vanadium from the leach solution which has a concentration of 1400 ppm (ug/L) vanadium.

Procedure.

1. Set up an apparatus to handle 6 separatory funnels.
2. Set up a pH meter and calibrate it using pH 7 and pH 10 buffer solutions.
3. Measure the pH of the vanadium leach solution.
4. Using a 1000 ml buret, add 100 ml of vanadium leach solution to each of 3 separatory funnels.
5. To the first separatory funnel add 10 ml of Aliquat 336 using a 250 ml buret. Label the funnel. Place a stopper into the funnel and mix by inverting several times. Place the funnel into the ring stand and allow the amine phase to separate from the aqueous phase for 3 hours.
- 5a. Slowly drain 30 to 40 ml of the aqueous portion (lower liquid in the separatory funnel) into a sample bottle. Label the bottle with the pH and the volume(ml) of Aliquat 336 used in the extraction.
6. Repeat step 5 with the second separatory funnel except add 20 ml of Aliquat 336.
7. Repeat step 5 with the third separatory funnel except add 40 ml of Aliquat 336.
8. Pour 400 ml of the vanadium leach solution into each of 3 separate 600 ml beakers.
9. Adjust the pH of the V leach solution in one of the beakers to pH 10 using 3 molar sulfuric acid. Stir the sample using a magnetic stirrer while adjusting the pH. Adjust the pH of the solution in the second beaker to a pH of 7 and the solution in the third beaker to a pH of 4.5. Record the pH of each solution, the volume(ml) of sulfuric acid used to neutralize, and then label each beaker with the pH. Cover the beakers with plastic and a rubber band.
10. Repeat steps 4 - 7 using the pH 10 solution, the pH 7 solution and the pH 4.5 solution.

NOTE: There should be a total of 12 samples. Three amine volume at four different pH values.

Solution Disposition.

After each test is complete, discharge the remainder of the aqueous portion of the solution into a beaker. This can be disposed of in the acid barrel.

The organic portion of the sample should be drained into a glass bottle and covered until the tests are complete. The final disposition of the organic will be in the waste organic solvent barrel.

Solvent Extraction of Precipitate Filtrate

An amine named Aliquat 336 is used to extract the vanadium from the red cake filtrate solution which has a concentration of 66 ppm (ug/L) vanadium.

Procedure.

1. Using a graduated cylinder, add 75 ml of red cake solution to a separatory funnel.
2. Add 30 ml of Aliquat 336 to the separatory funnel containing the red cake solution. Label the funnel. Place a stopper into the funnel and mix by inverting several times. Place the funnel into the ring stand and allow the amine phase to separate from the aqueous phase for 3 hours.
3. Slowly drain 30 to 40 ml of the aqueous portion (lower liquid in the separatory funnel) into a sample bottle. Label the sample as red cake solvent extraction. Submit the sample for ICP analysis.

Solution Disposition.

After each test is complete, discharge the remainder of the aqueous portion of the solution into a beaker. This can be disposed of in the acid barrel.

The organic portion of the sample should be drained into a glass bottle and covered until the tests are complete. The final disposition of the organic will be in the waste organic solvent barrel.