

**Final Report**

**THE REDUCTION OF FLUORIDE  
DISSOLUTION DURING INDURATION  
OFF-GAS SCRUBBING**

**COLERAINE MINERALS RESEARCH LABORATORY**

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## Abstract

A research project supported by the Minnesota Department of Natural Resources and the Iron Ore Cooperative Research Committee was undertaken to reduce the dissolution of fluoride into process water during taconite processing. Leach tests were conducted using rod mill feed samples and water containing varying concentrations of calcium and sodium. Laboratory liberation grinds were performed to evaluate fluoride rejection during grinding and magnetic separation. Tube furnace tests were conducted to evaluate fluoride volatilization during pellet induration. The results indicate that fluoride concentration of process water is a function of both calcium and sodium concentration in process water. It appears that less than 1 percent of the fluoride present in rod mill feed will dissolve in process water during grinding. More than 90 percent of the fluoride present in rod mill feed is rejected with tailings during size reduction and magnetic separation. The furnace tests demonstrate that bentonite and fluxstone (calcite and dolomite) addition to taconite concentrate during pellet production increases the amount of fluoride that volatilizes during induration. Lime hydrate addition to pellets decreases the amount of fluoride that volatilizes during pellet induration. During acid pellet production approximately three times more fluoride enters the water during induration-off-gas scrubbing than during grinding. When fluxed pellets are produced three to eight times more fluoride enters the water during off-gas scrubbing than during taconite grinding.

## Introduction

Minnesota taconite facilities have been operating for nearly 40 years. During this time the concentration of dissolved solids in the recycled process water has increased. This increase in the ionic strength of the process water has occurred because of the following four mechanisms: 1) sulfide mineral oxidation, 2) acid neutralization by carbonate salts, 3) dissolution of soluble salts, and 4) removal of soluble gases from the induration exhaust by the wet scrubbers.

The introduction of fluoride into taconite process water is accomplished by the dissolution of soluble fluoride salts during grinding and also by the removal of soluble fluoride gases from the induration exhaust by the wet scrubbers.<sup>1</sup>

The concern with fluoride is environmental rather than process related. Water containing high fluoride concentration can be harmful to both humans and wildlife. Water containing less than 2 mg/L (ppm) is generally considered safe for human consumption. The US EPA has set a secondary drinking water standard of 2 ppm fluoride and an enforceable drinking water standard of 4 ppm fluoride.<sup>2,3</sup>

## Acknowledgments

This study was funded by the Minnesota Department of Natural Resources and the Iron Ore Cooperative Research Committee, whose support is gratefully acknowledged. We

would like to extend our thanks to LTV Mining and Minntac for providing samples for this study.

### **Background**

The main objectives of this study were to: 1) Determine what happens to fluoride minerals during taconite grinding and magnetic separation, 2) Determine how much fluoride is volatilized during pellet induration, and 3) Determine methods to reduce the amount of fluoride mineral dissolved during grinding and volatilized during induration.

A previous study conducted by the Coleraine Minerals Research Laboratory demonstrated that the concentration of fluoride in process water decreases as the concentration of calcium increases. The study also demonstrated that the concentration of fluoride in process water increases as the concentration of sodium increases. Fluoride can be precipitated from solution by treating process water with various types of calcium salts such as calcium phosphate, calcium hydroxide, calcium carbonate (calcite) and calcium-magnesium carbonate (dolomite). Fluoride can also be removed through anion exchange in a biological peat filter.<sup>1</sup>

One method that can be used to inhibit fluoride dissolution during grinding and induration is to provide enough available calcium to form calcium fluoride during both grinding and induration. Any fluoride that dissolves during grinding should immediately react to form an insoluble calcium fluoride precipitate. The presence of available calcium in greenballs provides the prospect of calcium fluoride formation upon decomposition of fluoride minerals during induration. Calcium fluoride has a melting point of 2600 F and a boiling point of 4500 F and is not as volatile as most fluoride minerals.

### **Test Program**

**Flask-Leach Tests.** Several hundred grams of both LTV rod-mill-feed and Minntac rod-mill-feed were dry-pulverized to 100 percent passing 200 mesh. Pulverized rod-mill-feed samples ranging from 5 grams to 100 grams were placed into 300 ml Erlenmeyer flasks. The rod-mill-feed samples were leached with three different sodium solutions and three different calcium solutions. A leach volume of 150 ml was used for each test. The solutions were filtered and analyzed for calcium, sodium, fluoride, and pH. A description of each flask-leach test is given in Appendix 1.

**Liberation Grind Tests.** Standard liberation grind tests followed by magnetic Davis tube separations were conducted using both LTV rod-mill-feed and Minntac rod-mill-feed. The ground solids were analyzed for size prior to magnetic separation. Davis tube concentrates were analyzed for iron, silica and fluoride. A description of each liberation grind test is provided in Appendix 2.

**Vertical-Tube Furnace Tests.** Acid filter cake samples were obtained from LTV Mining and Minntac. Green pellets were made using bentonite, lime hydrate, and fluxstone (50% dolomite and 50% calcite). The green pellets were dried and fired at 800° C (1472° F),

900°C ( 1652° F), 1000° C (1832° F), 1100° C (2012° F), and 1200°C (2192° F) in a Burnell 2.5-inch diameter vertical-tube furnace capable of attaining a temperature of 1500° C. During firing, four pellets were suspended in a platinum basket. An air flow of 1 liter per minute passed through the furnace. Most firing tests were run for 20 minutes. Upon completion of a test, the pellet samples were pulverized and analyzed for iron, silica, calcium, magnesium, fluoride and magnetic iron (Satmagan). A description of each vertical-tube-furnace-firing test is listed in Appendix 3.

### Discussion of Results

Flask-Leach Tests. The results of the flask-leach tests demonstrate that a high concentration of calcium in process water inhibits fluoride dissolution. The fluoride concentration in water from LTV-RMF-flask-leach tests was 0.62 ppm with 1000 ppm sodium and 0.33 ppm with 1000 ppm calcium. The results of the Minntac-RMF-flask-leach tests demonstrate that leach water containing 1000 ppm sodium contained 0.52 ppm fluoride and leach water containing 1000 ppm calcium contained 0.28 ppm fluoride. The results of the LTV and Minntac flask-leach-tests are given in Tables 1 and 2 respectively. The results of the flask-leach tests are illustrated in Figures 1 and 2. The amount of fluoride dissolved during the flask-leach tests is generally less than 1 percent of the fluoride contained in the RMF samples. This indicates that the fluoride minerals that occur in taconite are not very soluble.

Liberation Grind Tests. The liberation-grind-test results are given in Table 3. The liberation grind data indicate that 93 to 95 percent of the fluoride present in rod-mill-feed (RMF) is rejected to tailings when the grind is 80 percent minus 270 mesh. The data also indicate that grinding finer than 80 percent minus 270 mesh does very little to increase the rejection of fluoride to the tailings. Figures 3 and 4 illustrate the liberation of fluoride with respect to size and time respectively. Figure 5 illustrates the rejection of fluoride to the tails. LTV-rod-mill-feed has 0.013 percent fluoride and Minntac-rod-mill feed contains 0.006 percent fluoride.

Vertical-Tube Furnace Tests. Minntac filter cake used for green-pellet feed contained an average of 0.0020 percent fluoride. Minntac base-case acid pellets contained 0.0041 percent fluoride, which means that the bentonite used as the binder doubled the fluoride content of the pellet feed to the induration process. Minntac fully fluxed pellets containing fluxstone and bentonite have 0.0054 percent fluoride. Minntac pellets made with no bentonite and 1% lime hydrate contain 0.0030 percent fluoride and Minntac fully fluxed pellets made by using dolomite hydrate and lime hydrate contain 0.0029 percent fluoride. The Minntac fluxed pellet, which contains fluxstone and bentonite, volatilizes 0.080 ppm fluoride per degree Celsius between 800 C and 1200 C. This is the highest volatilization rate for any pellet tested. The Minntac base-case acid pellet has a volatilization rate of 0.027 ppm fluoride per degree Celsius (800 C to 1200 C). Minntac acid pellets made using 1 percent lime hydrate volatilize 0.034 ppm fluoride per degree Celsius ( 800 C to 1200 C). A Minntac fluxed pellet composed of dolomite hydrate and lime hydrate volatilized 0.052 ppm fluoride per degree Celsius (800 C to 1200 C). The use of dolomite hydrate and lime hydrate in a fully fluxed pellet rather than fluxstone reduced

fluoride volatilization by 35 percent. The standard Minntac acid pellet produced 66 percent less volatilized fluoride than the standard Minntac fluxed pellet. Fluoride volatilization using 1% lime hydrate as a binder rather than bentonite appeared to increase the volatilization rate of fluoride in an acid pellet ( 0.034 ppm/C rather than 0.027 ppm/C). The data for the Minntac tube furnace tests are found in Table 4. The data are illustrated in Figures 6 and 7. Figure 7 is a plot of the calculated linear regressions. The slopes of the lines on Figure 7 represent the amount of fluoride volatilized during each test. The steeper the slope, the higher the amount of fluoride volatilized during the test. Examination of both Figures 6 and 7 indicates that the use of lime hydrate in pellets rather than bentonite and/or fluxstone reduces the quantity of fluoride in green-pellet feed because the fluoride content of the lime hydrate is much lower than either bentonite or fluxstone.

LTV filter cake used for green-pellet feed contained an average of 0.0028 percent fluoride. LTV base-case acid pellets contained 0.0046 percent fluoride, which means that the bentonite used as the binder increased the fluoride content of the pellet feed by 0.0018 percent. LTV fully fluxed pellets containing fluxstone and bentonite have 0.0050 percent fluoride. LTV pellets made with no bentonite and 1% lime hydrate contain 0.0034 percent fluoride and LTV fully fluxed pellets made by using dolomite hydrate and lime hydrate contain 0.0043 percent fluoride. The LTV base-case acid pellet volatilized 0.042 ppm fluoride per degree Celsius between 800 C and 1200 C. This is the highest volatilization rate for any LTV pellet tested. The LTV pellet made with 1 percent lime hydrate rather than bentonite had a volatilization rate of 0.014 ppm fluoride per degree Celsius (800 C to 1200 C). LTV fully fluxed pellets made using limestone and bentonite had a volatilization rate of 0.035 ppm fluoride per degree Celsius (800 C to 1200 C). Fully fluxed LTV pellets composed of dolomite hydrate and lime hydrate volatilized 0.019 ppm fluoride per degree Celsius (800 C to 1200 C). The use of lime hydrate as a binder in LTV pellets rather than bentonite reduces fluoride volatilization by 67 percent (0.042 ppm/C to 0.014 ppm/C). The data for the LTV tube furnace tests are found in Table 5. The data are illustrated in Figures 8 and 9. Figure 9 is a plot of the calculated linear regressions. The slopes of the lines in Figure 9 represent the amount of fluoride volatilized during each test. The steeper the slope, the higher the amount of fluoride volatilized during the test. Examination of both Figures 8 and 9 indicates that the use of lime hydrate in pellets rather than bentonite and/or fluxstone reduces the quantity of fluoride in green-pellet feed because the fluoride content of the lime hydrate is much lower than either bentonite or fluxstone.

### **Fluoride Balance**

**Minntac Grinding and Furnace Tests.** Figure 10 contains a fluoride balance calculation that estimates the amount of fluoride that will dissolve in process water during grinding and induration. The amount fluoride that reports to process water during acid pellet production is estimated at 0.0054 to 0.0059 pounds of fluoride per long ton of rod mill feed processed. During fluxed pellet production this number would be 0.0136 to 0.0141 pounds of fluoride per long ton of rod mill feed processed. The concentrations of calcium and sodium in Minntac process water are 95 ppm and 75 ppm respectively and

therefore most of the fluoride that enters the process water precipitates as calcium fluoride.

LTV Grinding and Furnace Tests. Figure 11 contains a fluoride balance calculation that estimates the amount of fluoride that will dissolve in process water during grinding and induration. The quantity of fluoride that reports to process water during acid pellet production is estimated at 0.0081 to 0.0085 pounds of fluoride per long ton of rod mill feed processed. During fluxed pellet production this number would be 0.0070 to 0.0074 pounds of fluoride per long ton of rod mill feed processed. LTV Mining uses soda ash softening and has a much lower concentration of calcium in their process water than does Minntac. The concentrations of calcium and sodium in LTV process water are 17 ppm and 116 ppm respectively. Therefore the concentration of fluoride in process water will remain high because calcium fluoride precipitation will be inhibited.

### Observations

Calcium Fluoride Solubility. The solubility product ( $K_{sp}$ ) of calcium fluoride can be used to estimate the amount of fluoride that will remain in solution when a specified amount of calcium is in solution. Solubility calculations for calcium fluoride are given in Table 6. For LTV process water that contains 17 ppm calcium, the equilibrium concentration of fluoride at 25° C is 11.7 ppm fluoride. The actual concentration is 10.1 ppm. For Minntac process water that contains 95 ppm calcium, the equilibrium concentration of fluoride at 25° C is 4.9 ppm fluoride. The actual concentration is 2.8 ppm fluoride. In each case the fluoride concentration of the process water is slightly lower than the equilibrium concentration of fluoride at 25° C. Calcium fluoride is less soluble in cold water than in warm water. As the tailing basin water cools from summer to winter, calcium fluoride will precipitate. At 0° C, the equilibrium concentrations would be 8.0 ppm fluoride and 3.4 ppm fluoride for LTV and Minntac respectively. There are unit operations during the manufacture of fluxed pellets that introduce high concentrations of calcium into process water such as fluxed-pellet-chip grinding and fluxstone grinding. Fluxed-pellet-chip grinding water can contain 1000 ppm calcium and fluxstone grinding water can contain 300 ppm calcium. Process water exposed to these unit operations would readily precipitate calcium fluoride. Water containing 1000 ppm calcium could have less than 1 ppm fluoride, and water containing 300 ppm calcium could have less than 2 ppm fluoride. Minntac produces fluxed pellets and this could explain why the fluoride concentration in Minntac process water is below the equilibrium value.

Dissolution of Fluoride. It appears that sodium carbonate (soda ash) softening assists in the dissolution of fluoride minerals during grinding. The use of soda ash softening eliminates calcium from process water. This decrease in calcium concentration allows the fluoride concentration to increase by eliminating the formation of calcium fluoride precipitation. The use of soda ash also increases the concentration of sodium in process water which helps keep additional fluoride in solution.

Volatilization of Fluoride. Part of the reduction of fluoride in the green-pellets when using lime hydrate is due to dilution. The lime hydrate used in this research project



contained non-detectable quantities of fluoride. Commercial manufactures of lime hydrate and dolomite hydrate can make hydrates that contain extremely low concentrations of fluoride if they do not mix bag house dust with the product. Bag house dust can contain high concentrations of fluoride.

### Conclusions

1. Less than 1 percent of the fluoride present in taconite rod-mill-feed dissolved in process water during grinding.
2. High concentrations of calcium in grinding water deter the dissolution of fluoride during grinding.
3. High concentrations of sodium in grinding water aid in the dissolution of fluoride during grinding.
4. Over 90 percent of fluoride present in the taconite rod-mill-feed was rejected to tailings during grinding and magnetic separation.
5. Grinding rod-mill-feed samples finer than 80 percent passing 270 mesh does not provide additional rejection of fluoride during magnetic separation.
6. A fully fluxed pellet composed of Minntac acid filter cake, lime hydrate, and dolomite hydrate produced 35 percent less volatilized fluoride during induration than did a fully fluxed pellet composed of Minntac acid filter cake, fluxstone (calcite and dolomite), and bentonite.
7. A standard Minntac acid pellet, which contained Minntac acid filter cake and bentonite, produced 66 percent less volatilized fluoride during induration than a standard Minntac fluxed pellet, which contained Minntac acid filter cake, fluxstone and bentonite.
8. The use of lime hydrate with LTV filter cake reduced the amount of fluoride that was volatilized during pellet induration.
9. The use of lime hydrate as the binder in an acid LTV pellet, rather than bentonite, reduced fluoride volatilization by 67 percent during pellet induration.
10. The fluoride minerals that were present in LTV Mining filter cake appeared to be more susceptible to treatment with lime hydrate to reduce fluoride volatilization than were the fluoride minerals in Minntac filter cake.
11. The amount of fluoride in acid green-pellet feed when using bentonite as the pellet binder is 30 to 35 percent higher than when using lime hydrate as the pellet binder.

12. The amount of fluoride in fluxed green-pellet feed when using bentonite and fluxstone is about 50 percent higher than when using lime hydrate and dolomite hydrate.
13. Bentonite clay contributes 40 to 50 percent of the fluoride in acid green-pellet feed.
14. Fluxstone and Bentonite clay contribute about 15 percent and 35 percent of the fluoride in fluxed green-pellet feed respectively.

1. J. Engesser, "The removal of Sulfate and Fluoride from Process Water – The Effect of Water Chemistry on Filtering and Flotation" Iron Ore Cooperative Research Project, Department of Natural Resources, March 16, 1998
2. 40 Code of Federal Regulations Ch 1 (7-1-00 Edition), "National Secondary Drinking Water Regulations", Part 143.3, page 613.
3. 40 Code of Federal Regulations Ch 1 (7-1-00 Edition), "National Primary Drinking Water Regulations", Part 141, Appendix B Subpt 1, page 555.

**Table 1**

**Minntac Rod Mill Feed Flask-Leach Test Results**

| Rod Mill Feed Plant | Treatment Solution (ppm, X) | RMF Mass,g | % Solids | Ca Conc. Ppm | Na Conc. ppm | pH   | F Conc. ppm | % F Dissolved |
|---------------------|-----------------------------|------------|----------|--------------|--------------|------|-------------|---------------|
| Minntac             | 1000 Na                     | 0          | 0.0      | 2.3          | 1070.6       | 6.27 | 0.00        | 0.000         |
| Minntac             | 1000 Na                     | 5          | 3.2      | 13.3         | 1063.9       | 8.41 | 0.08        | 0.200         |
| Minntac             | 1000 Na                     | 10         | 6.3      | 14.8         | 1058.1       | 8.73 | 0.09        | 0.225         |
| Minntac             | 1000 Na                     | 25         | 14.3     | 23.7         | 1048.1       | 8.57 | 0.20        | 0.500         |
| Minntac             | 1000 Na                     | 50         | 25.0     | 31.5         | 1028.6       | 8.38 | 0.31        | 0.775         |
| Minntac             | 1000 Na                     | 100        | 40.0     | 40.8         | 983.2        | 8.36 | 0.52        | 1.300         |
| Minntac             | 167 Na                      | 0          | 0.0      | 1.4          | 177.3        | 5.28 | 0.00        | 0.000         |
| Minntac             | 167 Na                      | 5          | 3.2      | 10.2         | 172.3        | 7.29 | 0.00        | 0.000         |
| Minntac             | 167 Na                      | 10         | 6.3      | 20.8         | 168.9        | 8.08 | 0.01        | 0.025         |
| Minntac             | 167 Na                      | 25         | 14.3     | 16.3         | 153.6        | 7.92 | 0.12        | 0.300         |
| Minntac             | 167 Na                      | 50         | 25.0     | 20.4         | 160.4        | 8.12 | 0.22        | 0.550         |
| Minntac             | 167 Na                      | 100        | 40.0     | 26.3         | 150.5        | 8.11 | 0.55        | 1.375         |
| Minntac             | 100 Na                      | 0          | 0.0      | 1.9          | 97.4         | 4.81 | 0.00        | 0.000         |
| Minntac             | 100 Na                      | 5          | 3.2      | 8.9          | 92.9         | 7.48 | 0.00        | 0.000         |
| Minntac             | 100 Na                      | 10         | 6.3      | 10.7         | 88.7         | 7.92 | 0.01        | 0.035         |
| Minntac             | 100 Na                      | 25         | 14.3     | 13.3         | 84.4         | 8.06 | 0.11        | 0.268         |
| Minntac             | 100 Na                      | 50         | 25.0     | 16.5         | 79.6         | 8.05 | 0.18        | 0.455         |
| Minntac             | 100 Na                      | 100        | 40.0     | 19.1         | 62.0         | 8.29 | 0.32        | 1.200         |
| Minntac             | 1000 Ca                     | 0          | 0.0      | 1001.3       | 9.5          | 6.45 | 0.00        | 0.000         |
| Minntac             | 1000 Ca                     | 5          | 3.2      | 988.7        | 4.3          | 6.48 | 0.01        | 0.025         |
| Minntac             | 1000 Ca                     | 10         | 6.3      | 975.1        | 3.7          | 6.66 | 0.03        | 0.075         |
| Minntac             | 1000 Ca                     | 25         | 14.3     | 965.4        | 6.9          | 6.65 | 0.09        | 0.225         |
| Minntac             | 1000 Ca                     | 50         | 25.0     | 948.6        | 10.6         | 6.98 | 0.18        | 0.450         |
| Minntac             | 1000 Ca                     | 100        | 40.0     | 901.4        | 18.2         | 7.11 | 0.28        | 0.700         |
| Minntac             | 167 Ca                      | 0          | 0.0      | 177.7        | 0.0          | 5.37 | 0.00        | 0.000         |
| Minntac             | 167 Ca                      | 5          | 3.2      | 173.2        | 0.0          | 6.53 | 0.01        | 0.133         |
| Minntac             | 167 Ca                      | 10         | 6.3      | 171.8        | 0.0          | 6.79 | 0.15        | 0.188         |
| Minntac             | 167 Ca                      | 25         | 14.3     | 164.9        | 1.6          | 6.97 | 0.18        | 0.333         |
| Minntac             | 167 Ca                      | 50         | 25.0     | 150.0        | 5.2          | 7.23 | 0.31        | 0.533         |
| Minntac             | 167 Ca                      | 100        | 40.0     | 131.9        | 10.2         | 7.41 | 0.50        | 0.890         |
| Minntac             | 100 Ca                      | 0          | 0.0      | 101.7        | 1.6          | 6.55 | 0.00        | 0.000         |
| Minntac             | 100 Ca                      | 5          | 3.2      | 96.5         | 2.6          | 7.19 | 0.05        | 0.025         |
| Minntac             | 100 Ca                      | 10         | 6.3      | 94.0         | 3.0          | 6.62 | 0.08        | 0.375         |
| Minntac             | 100 Ca                      | 25         | 14.3     | 90.7         | 5.0          | 6.92 | 0.13        | 0.450         |
| Minntac             | 100 Ca                      | 50         | 25.0     | 81.5         | 7.2          | 7.31 | 0.21        | 0.775         |
| Minntac             | 100 Ca                      | 100        | 40.0     | 74.2         | 10.5         | 7.55 | 0.36        | 1.025         |

**Table 2**

**LTV Rod Mill Feed Flask-Leach Test Results**

| Rod Mill Feed Plant | Treatment Solution (ppm, X) | RMF Mass.g | % Solids | Ca Conc. ppm | Na Conc. ppm | pH   | F Conc. Ppm | % F Dissolved |
|---------------------|-----------------------------|------------|----------|--------------|--------------|------|-------------|---------------|
| LTV Mining          | 1000 Na                     | 0          | 0.0      | 2.3          | 1058.1       | 6.56 | 0.00        | 0.000         |
| LTV Mining          | 1000 Na                     | 5          | 3.2      | 12.4         | 1043.8       | 8.95 | 0.03        | 0.035         |
| LTV Mining          | 1000 Na                     | 10         | 6.3      | 13.0         | 1035.2       | 8.93 | 0.07        | 0.081         |
| LTV Mining          | 1000 Na                     | 25         | 14.3     | 16.1         | 1033.5       | 8.83 | 0.20        | 0.231         |
| LTV Mining          | 1000 Na                     | 50         | 25.0     | 20.2         | 1028.8       | 8.59 | 0.41        | 0.473         |
| LTV Mining          | 1000 Na                     | 100        | 40.0     | 23.5         | 998.5        | 7.98 | 0.62        | 0.715         |
| LTV Mining          | 167 Na                      | 0          | 0.0      | 1.2          | 177.0        | 6.28 | 0.00        | 0.000         |
| LTV Mining          | 167 Na                      | 5          | 3.2      | 10.9         | 169.9        | 7.84 | 0.03        | 0.035         |
| LTV Mining          | 167 Na                      | 10         | 6.3      | 10.7         | 172.8        | 7.92 | 0.05        | 0.058         |
| LTV Mining          | 167 Na                      | 25         | 14.3     | 11.3         | 170.5        | 8.11 | 0.12        | 0.138         |
| LTV Mining          | 167 Na                      | 50         | 25.0     | 17.5         | 174.4        | 8.19 | 0.35        | 0.404         |
| LTV Mining          | 167 Na                      | 100        | 40.0     | 19.5         | 172.2        | 8.53 | 0.58        | 0.669         |
| LTV Mining          | 100 Na                      | 0          | 0.0      | 0.2          | 93.5         | 6.71 | 0.00        | 0.000         |
| LTV Mining          | 100 Na                      | 5          | 3.2      | 8.4          | 93.2         | 8.47 | 0.05        | 0.059         |
| LTV Mining          | 100 Na                      | 10         | 6.3      | 9.2          | 96.7         | 8.24 | 0.08        | 0.095         |
| LTV Mining          | 100 Na                      | 25         | 14.3     | 10.3         | 95.8         | 8.51 | 0.17        | 0.193         |
| LTV Mining          | 100 Na                      | 50         | 25.0     | 11.5         | 91.9         | 8.65 | 0.26        | 0.305         |
| LTV Mining          | 100 Na                      | 100        | 40.0     | 12.3         | 82.2         | 8.68 | 0.40        | 0.577         |
| LTV Mining          | 1000 Ca                     | 0          | 0.0      | 1006.7       | 0.9          | 5.83 | 0.00        | 0.000         |
| LTV Mining          | 1000 Ca                     | 5          | 3.2      | 985.1        | 4.4          | 6.59 | 0.05        | 0.053         |
| LTV Mining          | 1000 Ca                     | 10         | 6.3      | 971.1        | 7.0          | 6.61 | 0.07        | 0.083         |
| LTV Mining          | 1000 Ca                     | 25         | 14.3     | 955.2        | 13.9         | 6.98 | 0.14        | 0.157         |
| LTV Mining          | 1000 Ca                     | 50         | 25.0     | 910.2        | 26.0         | 7.12 | 0.22        | 0.249         |
| LTV Mining          | 1000 Ca                     | 100        | 40.0     | 848.4        | 37.5         | 7.19 | 0.33        | 0.376         |
| LTV Mining          | 167 Ca                      | 0          | 0.0      | 176.9        | 0.0          | 6.30 | 0.00        | 0.000         |
| LTV Mining          | 167 Ca                      | 5          | 3.2      | 169.4        | 0.3          | 6.72 | 0.00        | 0.000         |
| LTV Mining          | 167 Ca                      | 10         | 6.3      | 165.1        | 2.3          | 7.00 | 0.04        | 0.046         |
| LTV Mining          | 167 Ca                      | 25         | 14.3     | 150.0        | 8.4          | 7.27 | 0.12        | 0.138         |
| LTV Mining          | 167 Ca                      | 50         | 25.0     | 130.9        | 16.3         | 7.40 | 0.26        | 0.300         |
| LTV Mining          | 167 Ca                      | 100        | 40.0     | 101.7        | 30.6         | 7.50 | 0.48        | 0.554         |
| LTV Mining          | 100 Ca                      | 0          | 0.0      | 105.8        | 1.2          | 4.50 | 0.00        | 0.000         |
| LTV Mining          | 100 Ca                      | 5          | 3.2      | 99.6         | 3.6          | 6.51 | 0.05        | 0.058         |
| LTV Mining          | 100 Ca                      | 10         | 6.3      | 95.6         | 5.5          | 6.77 | 0.10        | 0.115         |
| LTV Mining          | 100 Ca                      | 25         | 14.3     | 80.3         | 10.1         | 6.96 | 0.29        | 0.335         |
| LTV Mining          | 100 Ca                      | 50         | 25.0     | 70.0         | 15.3         | 7.08 | 0.41        | 0.473         |
| LTV Mining          | 100 Ca                      | 100        | 40.0     | 43.0         | 24.0         | 7.73 | 0.58        | 0.669         |

**Table 3****Liberation Grind Data**

| <u>RMF Plant</u> | <u>(min) Time</u> | <u>% Fe</u> | <u>% SiO2</u> | <u>% F</u> | <u>% DT Recovery</u> | <u>% F Rejected</u> | <u>% -270</u> |
|------------------|-------------------|-------------|---------------|------------|----------------------|---------------------|---------------|
| Minntac          | 0.00              | 34.0        | 44.49         | 0.0060     |                      | 0.00                | 0.0           |
| Minntac          | 6.00              | 61.8        | 11.13         | 0.0030     | 33.2                 | 83.40               | 55.0          |
| Minntac          | 7.54              | 65.6        | 7.68          | 0.0020     | 30.7                 | 89.77               | 67.9          |
| Minntac          | 9.48              | 67.3        | 5.35          | 0.0010     | 29.2                 | 95.13               | 78.4          |
| Minntac          | 12.18             | 69.3        | 3.75          | 0.0010     | 28.9                 | 95.18               | 89.1          |
| Minntac          | 12.18             | 69.1        | 3.77          | 0.0010     | 28.7                 | 95.22               | 89.1          |
| Minntac          | 20.00             | 70.1        | 2.52          | 0.0010     | 27.8                 | 95.37               | 99.4          |
| Minntac          | 40.00             | 70.8        | 2.03          | 0.0005     | 27.5                 | 97.71               | 100.0         |
| LTV              | 0.00              | 31.5        | 47.98         | 0.0130     |                      | 0.00                | 0.0           |
| LTV              | 6.00              | 57.0        | 16.45         | 0.0090     | 36.4                 | 74.80               | 47.2          |
| LTV              | 9.12              | 64.8        | 9.41          | 0.0030     | 31.5                 | 92.73               | 67.4          |
| LTV              | 11.12             | 66.1        | 6.73          | 0.0030     | 29.9                 | 93.10               | 79.4          |
| LTV              | 14.00             | 67.7        | 5.53          | 0.0030     | 29.2                 | 93.26               | 89.7          |
| LTV              | 20.00             | 68.8        | 3.89          | 0.0020     | 26.9                 | 95.86               | 98.3          |
| LTV              | 40.00             | 70.1        | 2.74          | 0.0020     | 26.5                 | 95.92               | 100.0         |

**Table 4**

**Minntac Vertical Tube Furnace Test Data**

| <u>Sample Description</u>  | <u>Firing Time, min</u> | <u>Firing Temp, C</u> | <u>% F</u> | <u>% Fe</u> | <u>% SiO2</u> | <u>% CaO</u> | <u>% Mag Fe</u> | <u>% MgO</u> |
|----------------------------|-------------------------|-----------------------|------------|-------------|---------------|--------------|-----------------|--------------|
| Minntac Acid Filter Cake   |                         |                       | 0.0017     | 68.2        | 3.93          | 0.35         | 67.45           | 0.29         |
| Minntac Acid Filter Cake   |                         |                       | 0.0023     | 68.1        | 3.85          | 0.34         | 67.26           | 0.27         |
| Minntac Bentonite Clay     |                         |                       | 0.15       | 1.71        | 62.5          | 0.91         |                 | 0.75         |
| Fluxstone (50 – 50)        |                         |                       | 0.019      | 0.11        | 0.62          | 42.1         |                 | 11.3         |
| Minntac Base Acid Feed     |                         |                       | 0.0042     | 67.1        | 4.12          | 0.34         | 66.11           |              |
| Minntac Base Case Acid     | 20                      | 800                   | 0.0041     | 67.2        | 4.18          | 0.33         | 5.04            |              |
| Minntac Base Case Acid     | 20                      | 900                   | 0.0040     | 66.6        | 4.15          | 0.32         | 2.19            |              |
| Minntac Base Case Acid     | 20                      | 1000                  | 0.0038     | 66.5        | 4.21          | 0.33         | 0.15            |              |
| Minntac Base Case Acid     | 20                      | 1100                  | 0.0034     | 66.2        | 4.25          | 0.34         | 0.00            |              |
| Minntac Base Case Acid     | 20                      | 1200                  | 0.0030     | 66.4        | 4.21          | 0.34         | 0.00            |              |
| Minntac 1% Lime Feed       |                         |                       | 0.0031     | 66.2        | 3.65          | 1.60         | 65.16           |              |
| Minntac 1%Lime Pellet      | 20                      | 800                   | 0.0030     | 66.3        | 3.71          | 1.55         | 9.02            |              |
| Minntac 1%Lime Pellet      | 20                      | 900                   | 0.0019     | 66.1        | 3.75          | 1.65         | 0.67            |              |
| Minntac 1%Lime Pellet      | 20                      | 1000                  | 0.0018     | 66.0        | 3.62          | 1.72         | 0.00            |              |
| Minntac 1%Lime Pellet      | 20                      | 1100                  | 0.0018     | 65.8        | 3.78          | 1.79         | 0.00            |              |
| Minntac 1%Lime Pellet      | 20                      | 1200                  | 0.0014     | 65.9        | 3.76          | 1.73         | 0.00            |              |
| Minntac 1%Lime Pellet      | 20                      | 800                   | 0.0025     | 66.5        | 3.78          | 1.57         | 8.97            |              |
| Minntac 1%Lime Pellet      | 20                      | 1000                  | 0.0020     | 66.1        | 3.86          | 1.67         | 0.00            |              |
| Minntac 1%Lime Pellet      | 20                      | 1100                  | 0.0019     | 66.0        | 3.76          | 1.63         | 0.00            |              |
| Minntac 1%Lime Pellet      | 20                      | 1200                  | 0.0014     | 65.9        | 3.66          | 1.61         | 0.00            |              |
| Minntac Fluxstone Pel Feed |                         |                       | 0.0055     | 63.6        | 4.11          | 3.55         | 61.45           | 1.04         |
| Minntac Fluxstone Pellet   | 20                      | 800                   | 0.0054     | 63.9        | 4.18          | 3.63         | 17.11           | 1.08         |
| Minntac Fluxstone Pellet   | 20                      | 1000                  | 0.0047     | 63.6        | 4.16          | 3.75         | 1.10            | 1.14         |
| Minntac Fluxstone Pellet   | 20                      | 1100                  | 0.0033     | 64.1        | 4.19          | 3.60         | 1.00            | 1.13         |
| Minntac Fluxstone Pellet   | 20                      | 1200                  | 0.0023     | 63.4        | 4.10          | 3.43         | 0.49            | 1.10         |
| Minntac Flux Lime Feed     |                         |                       | 0.0032     | 63.7        | 3.55          | 3.44         | 61.22           | 1.07         |
| Minntac Flux Lime Pellet   | 20                      | 800                   | 0.0029     | 64.0        | 3.60          | 3.49         | 16.42           | 1.09         |
| Minntac Flux Lime Pellet   | 20                      | 1000                  | 0.0020     | 64.3        | 3.65          | 3.51         | 1.05            | 1.07         |
| Minntac Flux Lime Pellet   | 20                      | 1100                  | 0.0016     | 64.3        | 3.57          | 3.57         | 0.56            | 1.09         |
| Minntac Flux Lime Pellet   | 20                      | 1200                  | 0.0007     | 64.1        | 3.62          | 3.30         | 0.45            | 1.04         |

**Table 5**

**LTV Vertical Tube Furnace Test Data**

| <u>Sample Description</u> | <u>Firing Time, min</u> | <u>Firing Temp, C</u> | <u>% F</u> | <u>% Fe</u> | <u>% SiO2</u> | <u>% CaO</u> | <u>% Mag Fe</u> | <u>% MgO</u> |
|---------------------------|-------------------------|-----------------------|------------|-------------|---------------|--------------|-----------------|--------------|
| LTV Filter Cake           |                         |                       | 0.0028     | 68.1        | 4.82          | 0.45         | 66.89           | 0.31         |
| LTV Filter Cake           |                         |                       | 0.0027     | 67.8        | 4.77          | 0.48         | 66.74           | 0.29         |
| LTV Bentonite Clay        |                         |                       | 0.12       | 2.47        | 54.1          | 2.03         |                 | 0.33         |
| LTV Base Case Acid Feed   |                         |                       | 0.0045     | 67.2        | 5.21          | 0.44         | 65.21           |              |
| LTV Base Case Acid        | 10                      | 800                   | 0.0045     | 65.5        | 5.22          |              | 9.29            |              |
| LTV Base Case Acid        | 10                      | 900                   | 0.0044     | 67.6        | 5.29          |              | 0.03            |              |
| LTV Base Case Acid        | 10                      | 1000                  | 0.0039     | 67.7        | 5.31          | 0.43         | 0.01            |              |
| LTV Base Case Acid        | 10                      | 1100                  | 0.0038     | 65.6        | 5.26          | 0.43         | 0.00            |              |
| LTV Base Case Acid        | 10                      | 1200                  | 0.0024     | 66.0        | 5.36          | 0.45         | 0.00            |              |
| LTV Base Case Acid        | 20                      | 800                   | 0.0047     | 67.4        | 5.28          | 0.44         | 9.25            |              |
| LTV Base Case Acid        | 20                      | 900                   | 0.0039     | 64.8        | 5.25          |              | 1.12            |              |
| LTV Base Case Acid        | 20                      | 1000                  | 0.0040     | 65.4        | 5.27          | 0.43         | 0.00            |              |
| LTV Base Case Acid        | 20                      | 1100                  | 0.0032     | 65.6        | 5.31          | 0.43         | 0.07            |              |
| LTV Base Case Acid        | 20                      | 1200                  | 0.0029     | 65.2        | 5.30          | 0.44         | 0.00            |              |
| LTV 1% Lime Pellet Feed   |                         |                       | 0.0035     | 64.9        | 4.79          | 1.29         | 63.41           |              |
| LTV 1% Lime Pellet        | 20                      | 800                   | 0.0032     | 64.9        | 4.75          | 1.35         | 6.05            |              |
| LTV 1% Lime Pellet        | 20                      | 900                   | 0.0031     | 64.9        | 4.78          | 1.41         | 0.54            |              |
| LTV 1% Lime Pellet        | 20                      | 1000                  | 0.0028     | 64.9        | 4.82          | 1.38         | 0.22            |              |
| LTV 1% Lime Pellet        | 20                      | 1100                  | 0.0027     | 65.1        | 4.81          | 1.44         | 0.00            |              |
| LTV 1% Lime Pellet        | 20                      | 1200                  | 0.0027     | 64.7        | 4.78          | 1.42         | 0.22            |              |
| LTV 1%Lime Pellet         | 20                      | 800                   | 0.0037     | 66.8        | 4.84          | 1.33         | 7.52            |              |
| LTV 1%Lime Pellet         | 20                      | 1000                  | 0.0034     | 65.7        | 4.75          | 1.39         | 0.66            |              |
| LTV 1%Lime Pellet         | 20                      | 1100                  | 0.0024     | 65.8        | 4.76          | 1.43         | 0.00            |              |
| LTV 1%Lime Pellet         | 20                      | 1200                  | 0.0021     | 66.0        | 4.62          | 1.39         | 0.00            |              |
| LTV Fluxstone Pellet Feed |                         |                       | 0.0052     | 61.8        | 5.01          | 3.53         | 60.82           | 1.31         |
| LTV Fluxstone Pellet      | 20                      | 800                   | 0.0050     | 62.9        | 4.99          | 3.48         | 10.12           | 1.31         |
| LTV Fluxstone Pellet      | 20                      | 1000                  | 0.0042     | 63.1        | 4.91          | 3.55         | 0.85            | 1.28         |
| LTV Fluxstone Pellet      | 20                      | 1100                  | 0.0044     | 63.2        | 4.96          | 3.51         | 0.88            | 1.27         |
| LTV Fluxstone Pellet      | 20                      | 1200                  | 0.0035     | 63.0        | 4.99          | 3.61         | 1.26            | 1.31         |
| LTV Flux Lime Pellet Feed |                         |                       | 0.0041     | 62.4        | 4.61          | 3.51         | 61.21           | 1.15         |
| LTV Flux Lime Flux Pellet | 20                      | 800                   | 0.0043     | 63.1        | 4.68          | 3.66         | 9.22            | 1.21         |
| LTV Flux Lime Flux Pellet | 20                      | 1000                  | 0.0035     | 63.4        | 4.62          | 3.51         | 0.54            | 1.16         |
| LTV Flux Lime Flux Pellet | 20                      | 1100                  | 0.0034     | 63.0        | 4.70          | 3.50         | 0.55            | 1.19         |
| LTV Flux Lime Flux Pellet | 20                      | 1200                  | 0.0036     | 63.1        | 4.77          | 3.64         | 0.77            | 1.22         |

**Table 6**

**Solubility of Calcium Fluoride**

$$K_{sp} = [Ca^{++}][F]^{-2} = 1.61 \times 10^{-10} \text{ at } 25^{\circ} \text{ C} \text{ Note}$$

$$K_{sp} = [Ca^{++}][F]^{-2} = 7.54 \times 10^{-11} \text{ at } 0^{\circ} \text{ C} \text{ Note}$$

The concentrations for both calcium and fluoride in the above equations are in moles/liter.

**Assume Minntac water is at 25° C and has a concentration of 95 ppm calcium.**

$$[Ca^{++}] = 95/(1000 \cdot 40) = 0.002375 \text{ moles/liter} \rightarrow (1.61 \times 10^{-10})/0.002375 = [F]^{-2}$$
$$[F] = 0.000260 \text{ moles/liter} \times 19 \text{ g/mole} \times 1000 \text{ liters} = 4.9 \text{ ppm}$$

**Assume LTV water is at 25°C and has a concentration of 17 ppm calcium.**

$$[Ca^{++}] = 17/(1000 \cdot 40) = 0.000425 \text{ moles/liter} \rightarrow (1.61 \times 10^{-10})/0.000425 = [F]^{-2}$$
$$[F] = 0.0006155 \text{ moles/liter} \times 19 \text{ g/mole} \times 1000 \text{ liters} = 11.7 \text{ ppm}$$

**Assume Minntac water is at 0° C and has a concentration of 95 ppm calcium.**

$$[Ca^{++}] = 95/(1000 \cdot 40) = 0.002375 \text{ moles/liter} \rightarrow (7.54 \times 10^{-11})/0.002375 = [F]^{-2}$$
$$[F] = 0.000178 \text{ moles/liter} \times 19 \text{ g/mole} \times 1000 \text{ liters} = 3.4 \text{ ppm}$$

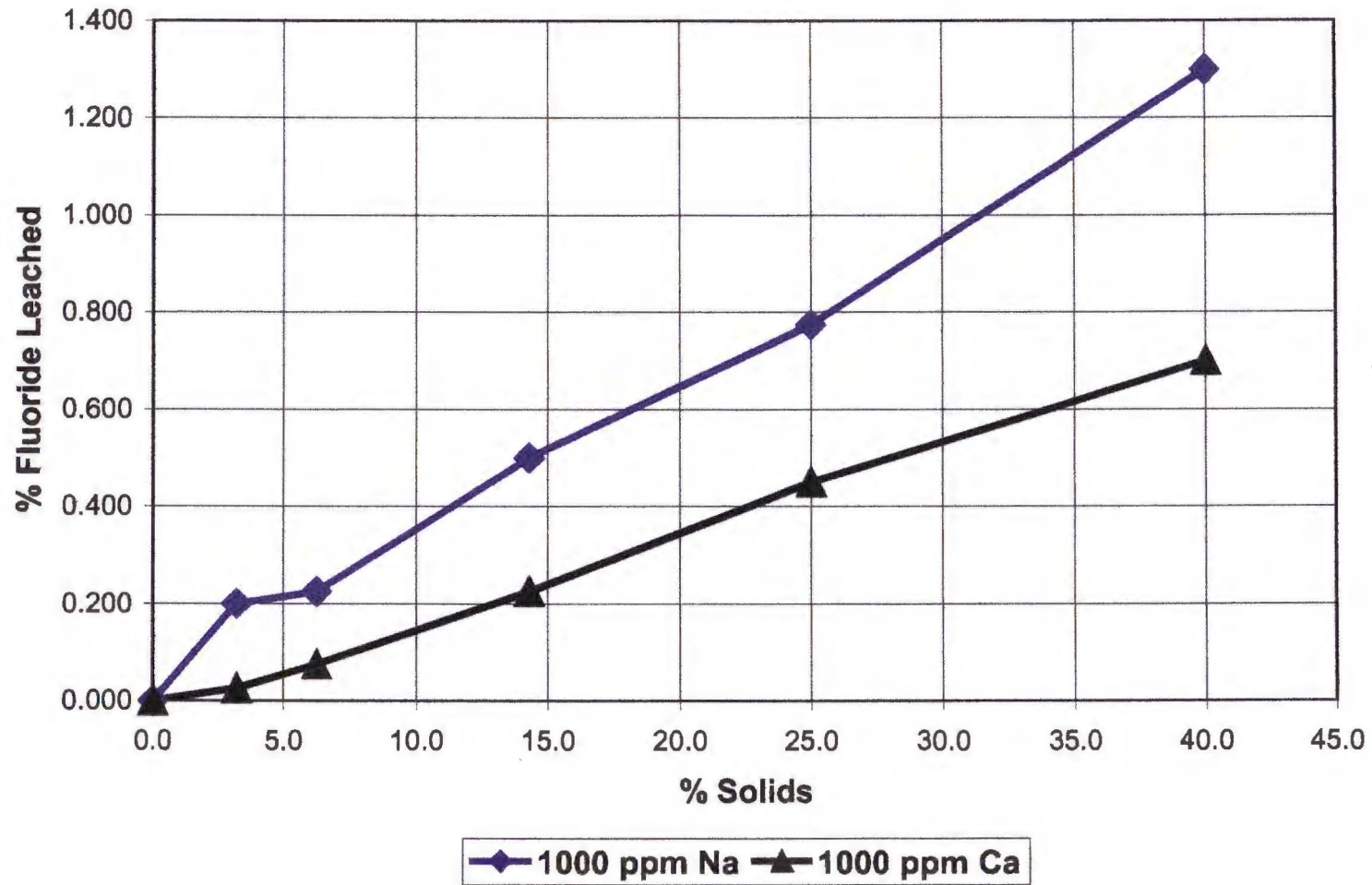
**Assume LTV water is at 0° C and has a concentration of 17 ppm calcium.**

$$[Ca^{++}] = 17/(1000 \cdot 40) = 0.000425 \text{ moles/liter} \rightarrow (7.54 \times 10^{-11})/0.000425 = [F]^{-2}$$
$$[F] = 0.0004212 \text{ moles/liter} \times 19 \text{ g/mole} \times 1000 \text{ liters} = 8.0 \text{ ppm F}$$

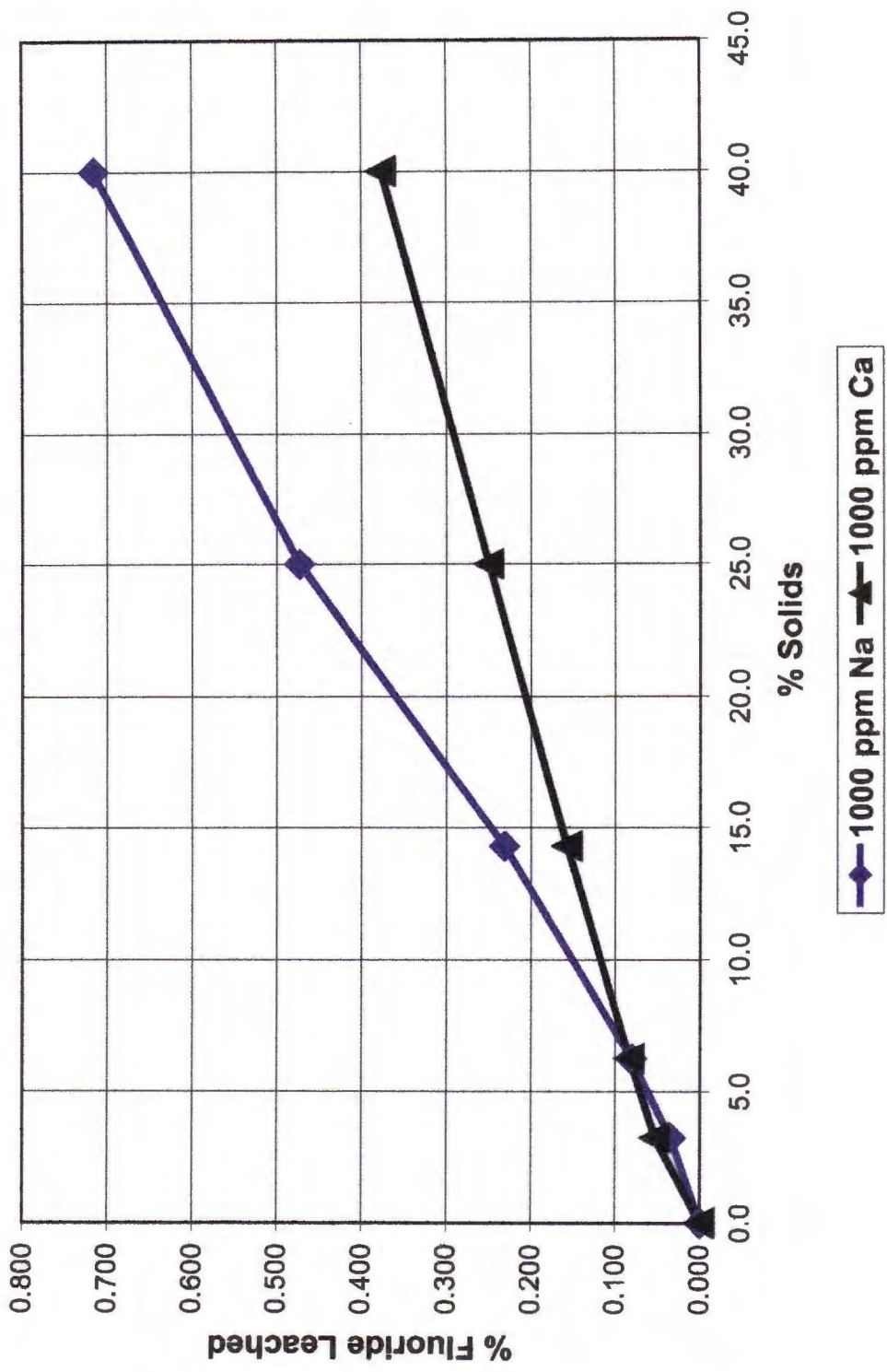
Note: 66<sup>th</sup> Edition - Handbook of Chemistry and Physics - CRC Press, 1985-1986.



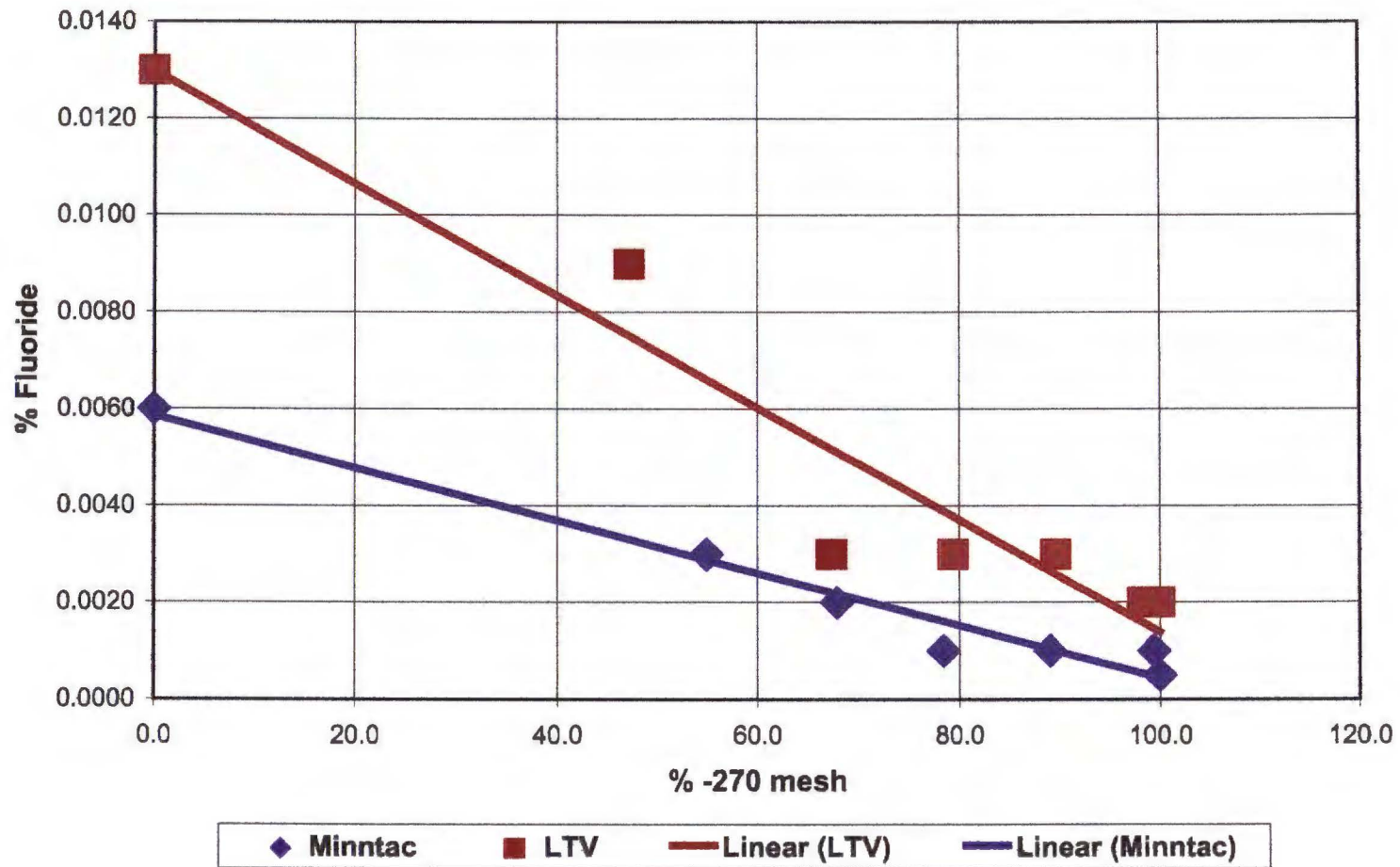
**Figure 1**  
**Fluoride Dissolution from Minntac Rod Mill Feed**



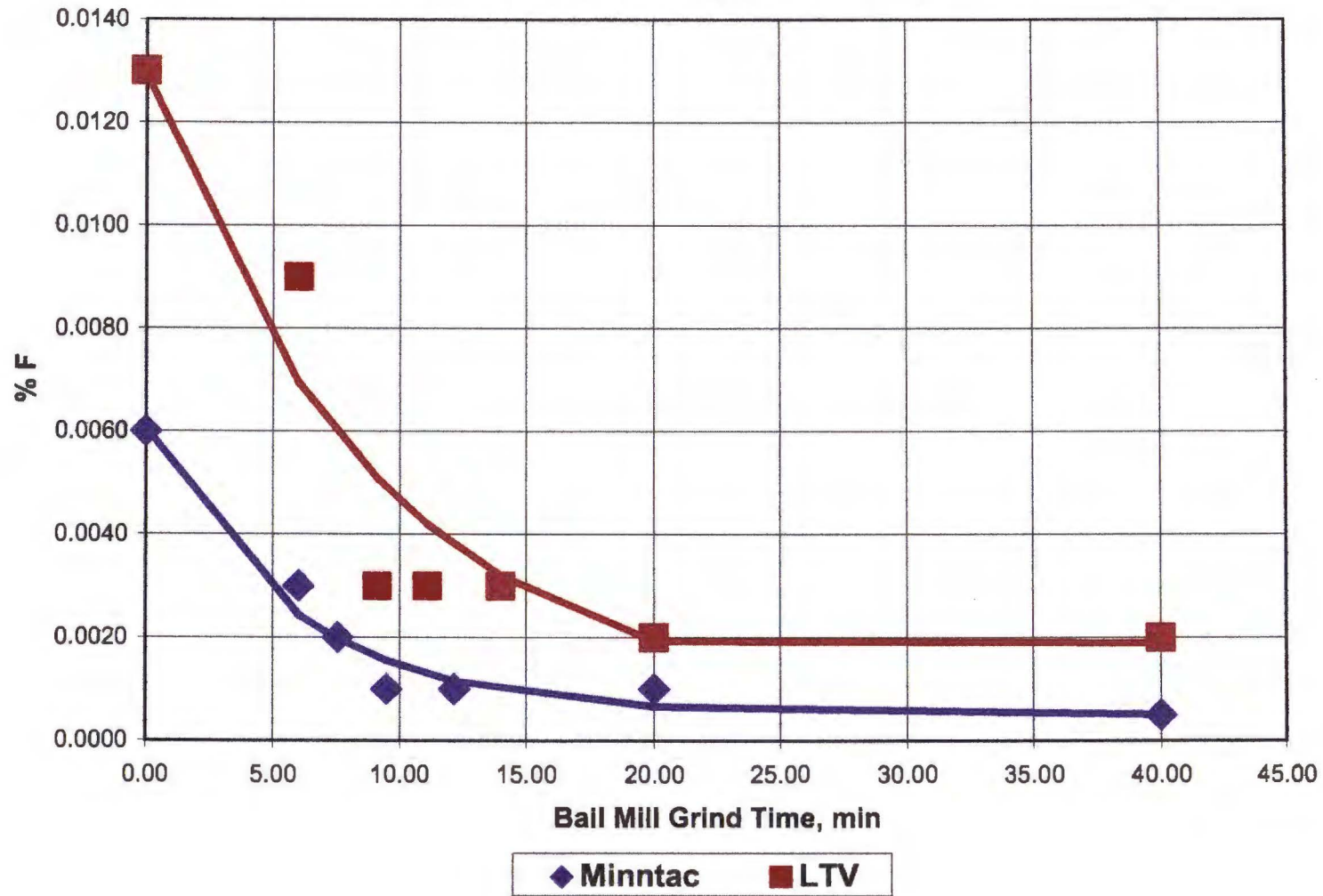
**Figure 2**  
**Fluoride Dissolution from LTV Rod Mill Feed**



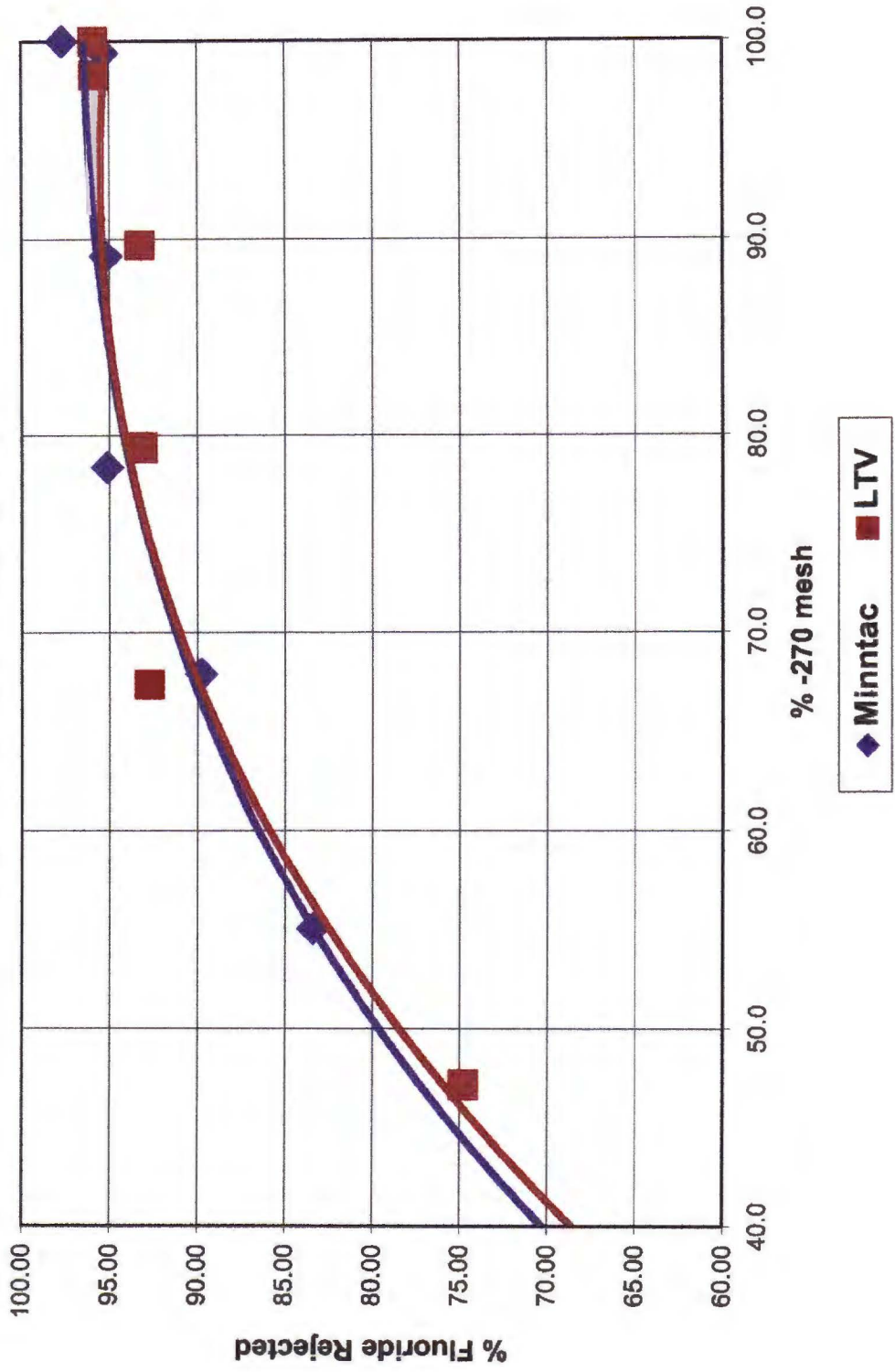
**Figure 3**  
**Fluoride in Davis Tube Concentrates**  
**Liberation Ball Mill Grinds of RMF**



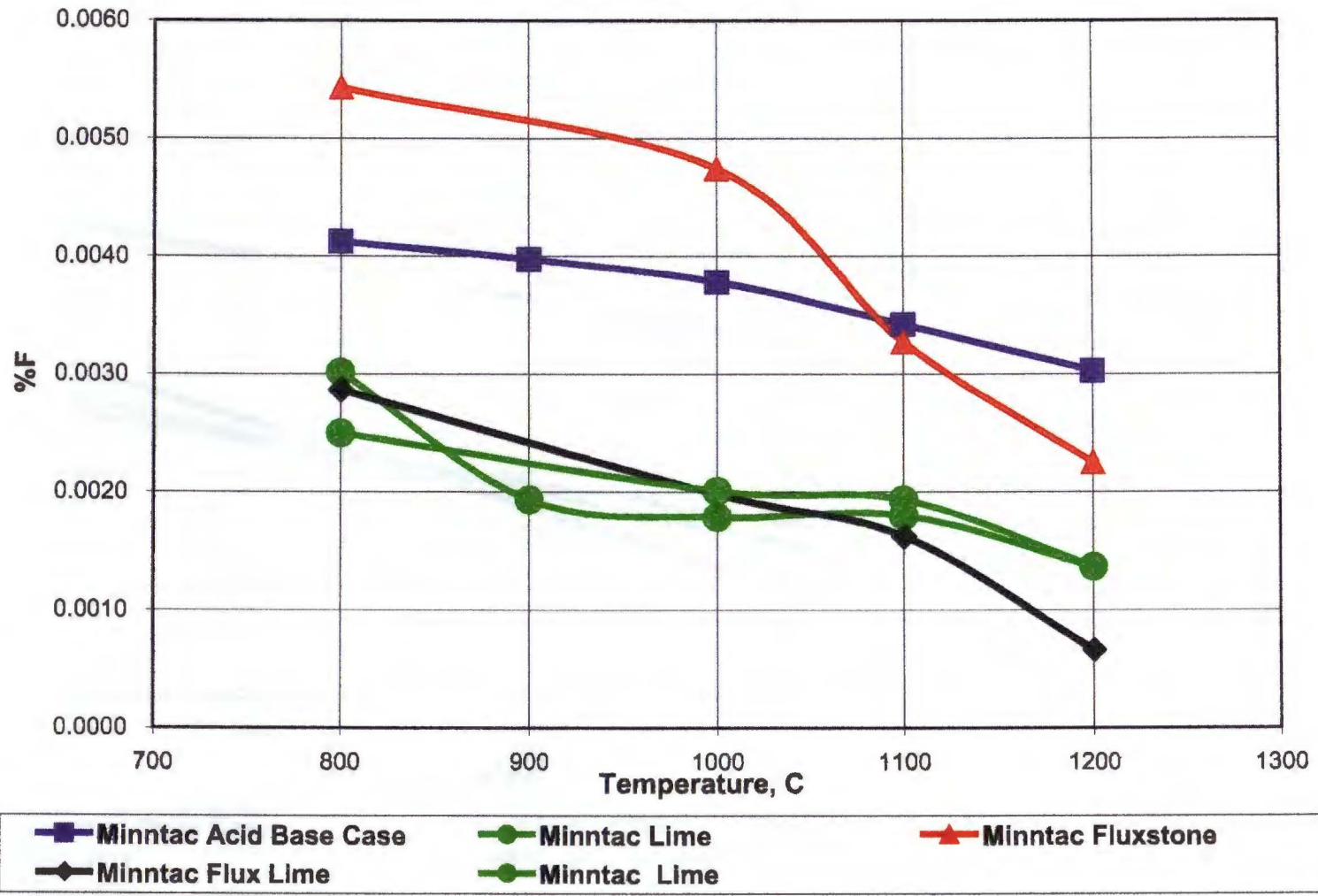
**Figure 4**  
**Fluoride in Davis Tube Concentrates**



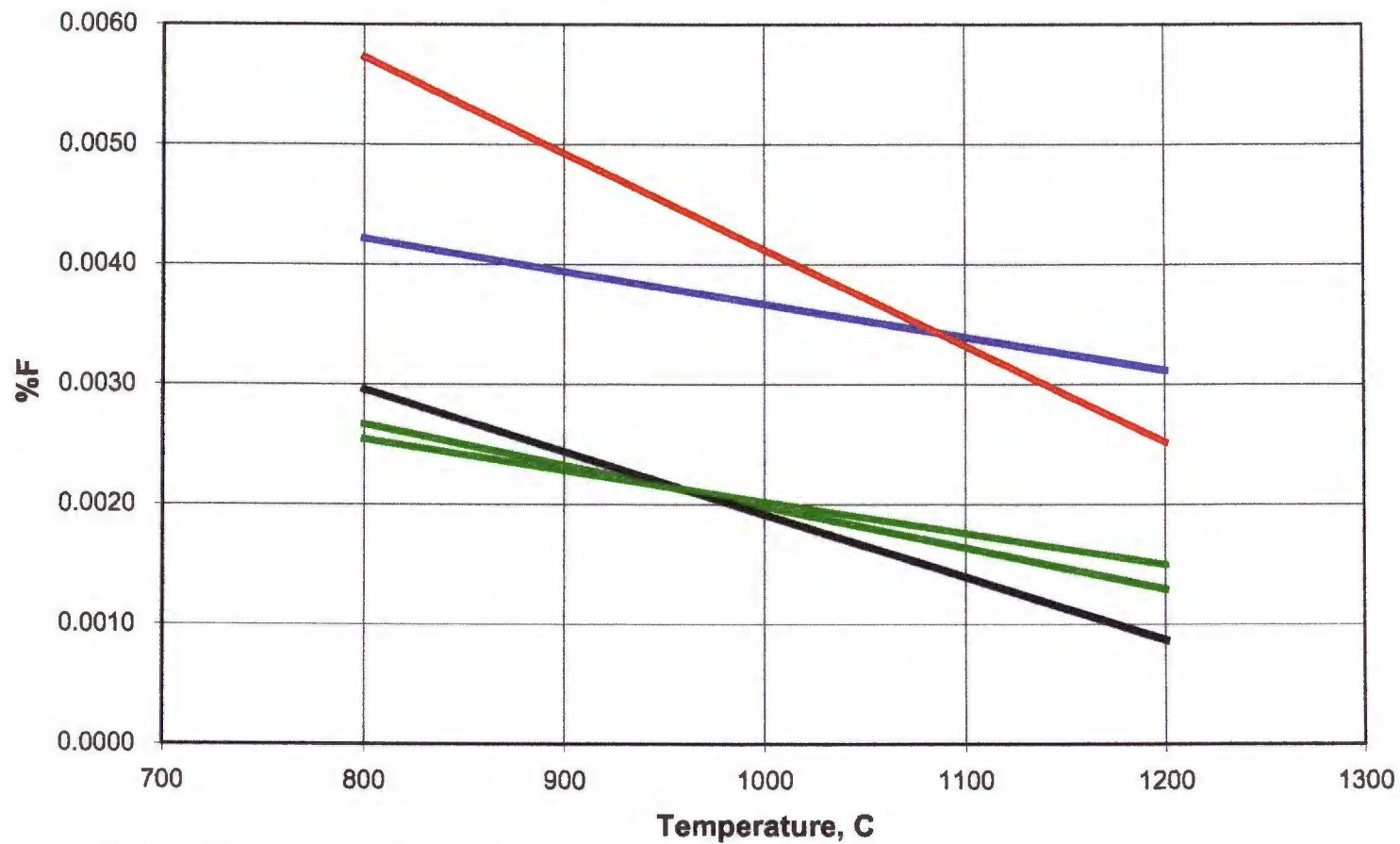
**Figure 5**  
**Fluoride Rejected In Davis Tube**  
**Liberation Ball Mill Grinds of RMF**



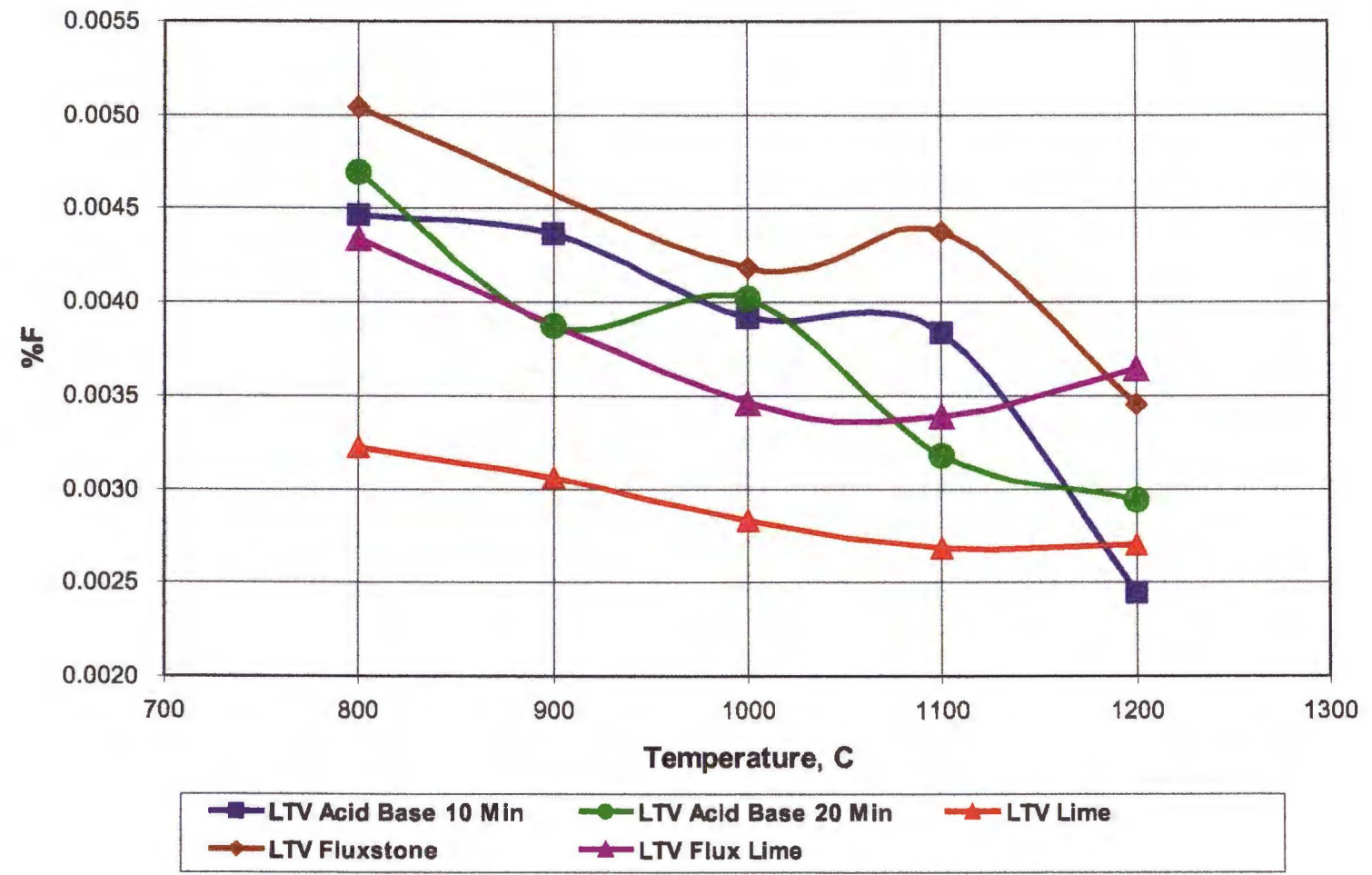
**Figure 6**  
**Minntac Fired Pellets**



**Figure 7**  
**Minntac Fired Pellets**

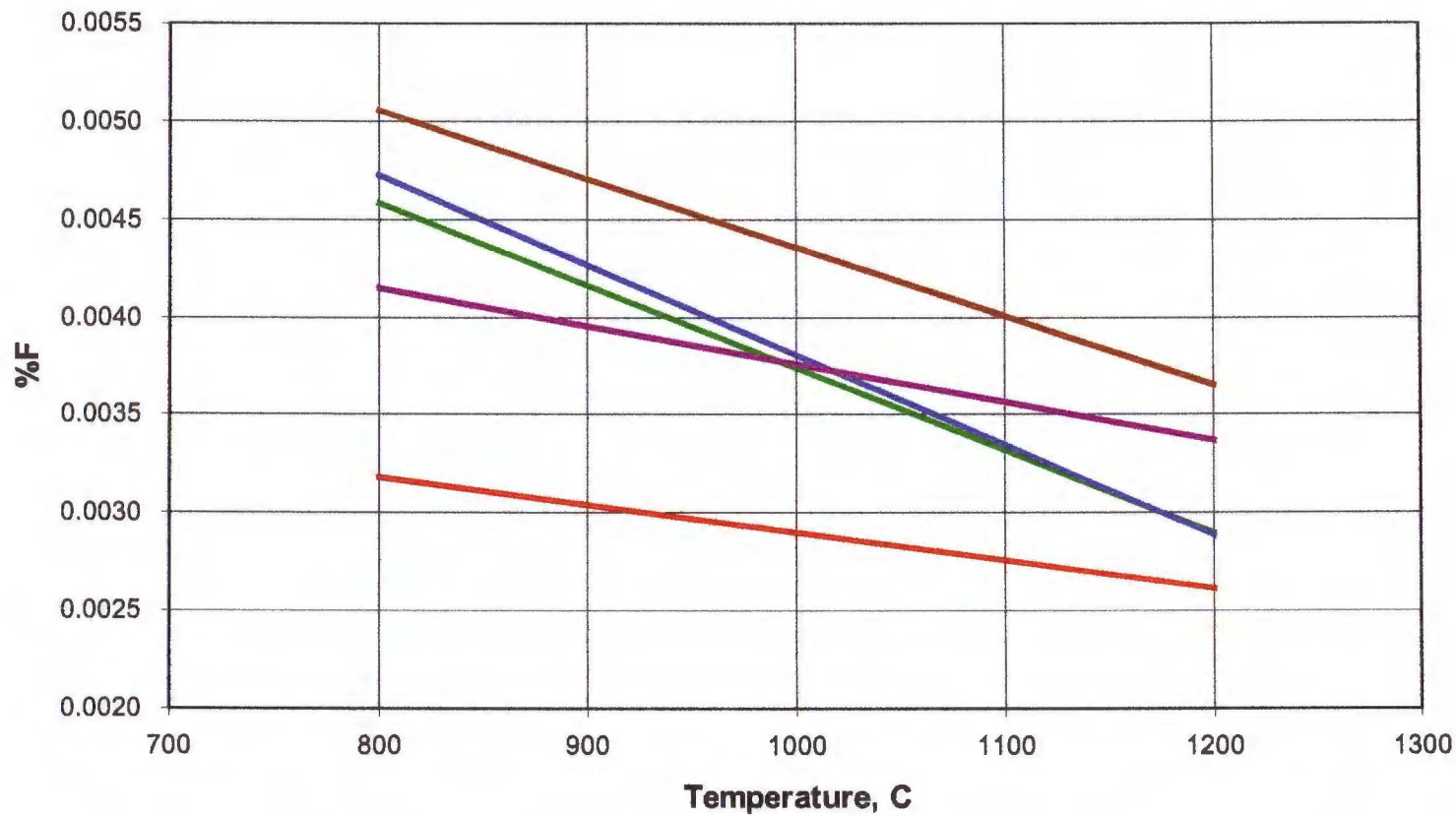


**Figure 8**  
**LTV Fired Pellets**





**Figure 9**  
**LTV Fired Pellets**



— Linear (LTV Fluxstone)      — Linear (LTV Acid Base 20 Min)      — Linear (LTV Acid Base 10 Min)  
— Linear (LTV Flux Lime)      — Linear (LTV Lime)

## Figure 10

### Minntac Fluoride Balance

#### Fluoride to Process Water During Grinding - High Calcium Grinding Water

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 0.00006 \text{ lb F/lb RMF} \times .00872 \text{ lb F to Water(Ca)} = \underline{\underline{0.00117 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water During Grinding - High Sodium Grinding Water

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 0.00006 \text{ lb F/lb RMF} \times .01292 \text{ lb F to Water(Na)} = \underline{\underline{0.00174 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water - 1200° C Acid Pellet Production – 60% Scrubber Efficiency

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 28.8 \% \text{ Recovery} \times (400 \times 0.027 \text{ lb F/1,000,000 lb RMF}) \times 60 \% \text{ scrub eff.} = \underline{\underline{0.00418 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water - 1200° C Fluxed Pellet Production – 60% Scrubber Efficiency

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 28.8 \% \text{ Recovery} \times (400 \times 0.080 \text{ lb F/1,000,000 lb RMF}) \times 60 \% \text{ scrub eff.} = \underline{\underline{0.0124 \text{ lb F/LT RMF}}}$$

## Figure 11

### LTV Mining Fluoride Balance

#### Fluoride to Process Water During Grinding - High Calcium Grinding Water

$$1 \text{ LTon RMF} \rightarrow 2240 \text{ lb RMF} \times 0.00013 \text{ lb F/lb RMF} \times .00533 \text{ lb F to Water(Ca)} = \underline{\underline{0.00155 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water During Grinding - High Sodium Grinding Water

$$1 \text{ LTon RMF} \rightarrow 2240 \text{ lb RMF} \times 0.00013 \text{ lb F/lb RMF} \times .00654 \text{ lb F to Water(Na)} = \underline{\underline{0.00190 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water - 1200° C Acid Pellet Production – 60% Scrubber Efficiency

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 29.2 \% \text{ Recovery} \times (400 \times 0.042 \text{ lb F/1,000,000 lb RMF}) \times 60 \% \text{ scrub eff.} = \underline{\underline{0.00659 \text{ lb F/LT RMF}}}$$

#### Fluoride to Process Water - 1200° C Fluxed Pellet Production – 60% Scrubber Efficiency

$$1 \text{ Lton RMF} \rightarrow 2240 \text{ lb RMF} \times 29.2 \% \text{ Recovery} \times (400 \times 0.035 \text{ lb F/1,000,000 lb RMF}) \times 60 \% \text{ scrub eff.} = \underline{\underline{0.00549 \text{ lb F/LT RMF}}}$$

## Appendix 1

### Flask-Leach Tests

Mix the following solutions:

**1000 ppm Sodium:** Weigh 2.543 grams of sodium chloride (NaCl) into a 600 ml beaker. Add 400 ml of deionized water and mix the sample on a magnetic stirrer until dissolved. Pour and rinse the contents of the beaker into a 1000 ml volumetric flask and bring the volume of water to the mark with deionized water. Pour the solution into a clean dry jar and label it 1000 ppm Na.

**1000 ppm Calcium:** Weigh 3.675 grams of calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) into a 600 ml beaker. Add 400 ml of deionized water and mix the sample on a magnetic stirrer until dissolved. Pour and rinse the contents of the beaker into a 1000 ml volumetric flask and bring the volume of water to the mark with deionized water. Pour the solution into a clean dry jar and label it 1000 ppm Ca.

### Minntac RMF Sodium (Na) Leach Tests

Tests 1 – 6 Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 150 ml of 1000 ppm Na solution to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

Tests 7 – 12 Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 25 ml of 1000 ppm Na solution and 125 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

Tests 13 – 18 Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 15 ml of 1000 ppm Na solution and 135 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

### **Minntac RMF Calcium (Ca) Leach Tests**

**Tests 19 – 24** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 150 ml of 1000 ppm Ca solution to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 25 – 30** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 25 ml of 1000 ppm Ca solution and 125 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 31 – 36** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **Minntac RMF** into six 300 ml Erlenmeyer flasks. Add 15 ml of 1000 ppm Ca solution and 135 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

### **LTV RMF Sodium (Na) Leach Tests**

**Tests 37 – 42** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **LTV RMF** into six 300 ml Erlenmeyer flasks. Add 150 ml of 1000 ppm Na solution to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 43 – 48** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **LTV RMF** into six 300 ml Erlenmeyer flasks. Add 25 ml of 1000 ppm Na solution and 125 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 49 – 54** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized **LTV RMF** into six 300 ml Erlenmeyer flasks. Add 15 ml of 1000 ppm Na solution and 135 ml of

deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

### **LTV RMF Calcium (Ca) Leach Tests**

**Tests 55 – 60** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized LTV RMF into six 300 ml Erlenmeyer flasks. Add 150 ml of 1000 ppm Ca solution to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 61 – 66** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized LTV RMF into six 300 ml Erlenmeyer flasks. Add 25 ml of 1000 ppm Ca solution and 125 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

**Tests 67 – 72** Weigh 0.00, 5.00, 10.00, 25.00, 50.00, and 100.00 grams of pulverized LTV RMF into six 300 ml Erlenmeyer flasks. Add 15 ml of 1000 ppm Ca solution and 135 ml of deionized water to each flask. Place a stopper on each flask and shake the flask and contents on a shaker-table for 1 hour. Remove the flask and contents from the shaker-table and filter the sample with a Buchner funnel using Whatman GAA filter paper and a clean dry side arm flask. Pour the filtered solution into a clean dry bottle and save for analysis. Analyze the solution for Ca, Na, pH, and F.

## **Appendix 2**

### **Liberation Grind Tests**

Crush the sample through 6 mesh. Mix and split out about 2 kilograms. Screen on a 20 mesh shaker-screen. Crush the plus 20 mesh material in a roll crusher until it all passes through the 20 mesh screen. Roll and mix thoroughly and riffle out about 1200 grams. Riffle into six samples and adjust each sample to 200 grams. Use a 200 gram sample and mix it with 100 ml of water. Place the slurry into the liberation grind mill with the correct ball charge. Initial grind the sample for 6 minutes. When the 200 gram sample has been ground the desired time the mill is dump the mill and contents into a coarse screen to hold the grinding balls. Clean and wash the grinding balls, mill and mill cover into the sample. Using wet screen and dry screen procedures, determine the % passing 270 mesh. Calculate the approximate grind times needed to obtain 75, 85, and 95 percent passing 270 mesh. In addition to the 3 calculated grind times, also perform liberation grinds for 20 minutes and a 40 minutes. Each grind is carried out with a 200 gram sample and the appropriate ball charge. Use wet screen and dry screen test procedures to determine the percent passing 270 mesh for each liberation grind. Recombined the +270 mesh and -270 mesh material from each screen analysis. Split out 10 grams from each liberation grind and run a Davis tube magnetic separation per the Davis Tube Procedure. Dry the Davis tube magnetic concentrate and submit for chemical analysis. Analyze each Davis tube concentrate for Fe, SiO<sub>2</sub>, and F.

Run the above tests with both Minntac rod-mill-feed and LTV rod-mill-feed.

## **Appendix 3**

### **Vertical Tube Furnace Tests**

**These tests will be run at 5 temperatures - 800C, 900C, 1000C, 1100C, and 1200C.**

The flow through the tube furnace during firing should be 1 liter/minute air. The quench(cooling) flow will be 1 liter / minute air. Run 4 pellets for each test. Use the platinum basket and a platinum wire to support the basket.

### **Minntac Furnace Tests**

#### **Tests 1 – 5 – Minntac Base Case Acid Pellets**

For tests 1 – 5 make greenballs using the following mix.

5940 grams of Minntac Acid Filter Cake (dry basis)  
60 grams of Minntac Bentonite

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 1** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 2 – 5** – Repeat the procedure for test 1 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 1 through 5 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

#### **Tests 6 – 10 – Minntac Acid Pellets Bound with Lime**

For tests 6 – 10 make greenballs using the following mix.

5940 grams of Minntac Acid Filter Cake (dry basis)  
60 grams of Lime hydrate

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 6** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets



into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 7 – 10** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 6 through 10 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

**Tests 11 – 15** – Repeat tests 6, 7, 8, 9, and 10. Pulverize the pellets from tests 11 – 15 and submit them for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO and Mag Fe (by Satmagan).

### **Tests 16 – 20 – Minntac Fluxed Pellets with Fluxstone and Bentonite**

For tests 16 – 20 make greenballs using the following mix.

5460 grams of Minntac Acid Filter Cake (dry basis)  
480 grams of Minntac Fluxstone (dry basis)  
60 grams of Bentonite

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 16** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 17 – 20** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 16 through 20 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

### **Tests 21 – 25 – Minntac Fluxed Pellets with Lime hydrate and Dolomite hydrate**

For tests 21 – 25 make greenballs using the following mix.

5656 grams of Minntac Acid Filter Cake (dry basis)  
166 grams of Dolomite Hydrate  
178 grams of Lime Hydrate

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 21** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 22 – 25** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 21 through 25 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

## **LTV Mining Furnace Tests**

### **Tests 26 - 30 – LTV Base Case Acid Pellets**

For tests 26 – 30 make greenballs using the following mix.

5940 grams of LTV Acid Filter Cake (dry basis)

60 grams of LTV Bentonite

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 26** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 27 – 30** – Repeat the procedure for test 1 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 26 through 30 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

**Tests 31 – 35** – Repeat tests 26, 27, 28, 29, and 30. Pulverize the pellets from tests 31 – 35 and submit them for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO and Mag Fe (by Satmagan).

### **Tests 36 – 40 – LTV Acid Pellets Bound with Lime**

For tests 36 – 40 make greenballs using the following mix.

5940 grams of LTV Acid Filter Cake (dry basis)

60 grams of Lime hydrate

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 36** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 37 – 40** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 36 through 40 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

**Tests 41 – 45** – Repeat tests 36, 37, 38, 39, and 40. Pulverize the pellets from tests 41 – 45 and submit them for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO and Mag Fe (by Satmagan).

### **Tests 46 – 50 – LTV Fluxed Pellets with Fluxstone and Bentonite**

For tests 46 – 50 make greenballs using the following mix.

5460 grams of LTV Acid Filter Cake (dry basis)

480 grams of LTV Fluxstone (dry basis)

60 grams of Bentonite

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 46** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 47 – 50** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 46 through 50 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).

### **Tests 51 – 55 – LTV Fluxed Pellets with Lime hydrate and Dolomite hydrate**

For tests 51 – 55 make greenballs using the following mix.

5656 grams of LTV Acid Filter Cake (dry basis)

166 grams of Dolomite Hydrate

178 grams of Lime Hydrate

Dry the greenballs. Pulverize several greenballs and save for chemical analysis.

**Test 51** – Place 4 greenballs into the platinum basket and lower it into the vertical tube furnace that has been preheated to 800 C. Roast the pellets for 20 minutes using 1 liter per minute cooling air. When the 20 minute roasting time is complete, lower the platinum basket and pellets into the cooling zone. Allow the pellets to cool for 5 minutes while continuing the 1 liter/minute air flow. Remove the fired pellets from the furnace. Pulverize and save for chemical analysis.

**Tests 52 – 55** – Repeat the procedure for test 6 at 900 C, 1000 C, 1100 C and 1200 C.

Submit the initial pulverized dry balls and the pulverized pellets from tests 51 through 55 for chemical analysis. Analyze for F, Fe, SiO<sub>2</sub>, CaO, MgO, and Mag Fe (by Satmagan).