0. EXECUTIVE SUMMARY

The *research reported will be applied* in the environmental review and permitting of future nonferrous mines in Minnesota, particularly those in the Duluth Complex. These regulatory activities require prediction of solute release from waste rock during mine operation and in the decades and centuries following mine closure. As a foundation for such predictions, the reactions occurring in waste rock stockpiles and variables affecting these reactions must be understood. This knowledge and a description of the proposed method of waste rock disposal are necessary to 1) design appropriate tests for predicting the release of potential pollutants from waste rock, 2) extrapolate results of such tests to field conditions, and 3) if necessary, implement mitigation measures that will ensure that water resources are not adversely impacted. In the present project, laboratory studies were conducted to examine solute release and variables affecting this release from waste rock from the South Kawishiwi intrusion (SKI) of the Duluth Complex. This study provides scientific and technical information necessary to address questions inherent to environmental review and permitting of nonferrous metal mines. The project also provides empirical data describing up to 24 years of rock dissolution for comparison with and extrapolation of data submitted for environmental review and permitting by companies proposing mining in the Duluth Complex.

The *objectives* of the study were as follows.

1) Determine the variation of laboratory drainage pH with solid-phase sulfur content of Duluth Complex samples.
2) Based on the aforementioned relationship, categorize solids based on sulfur content and associated drainage pH.
3) Determine the variation of major ion release rates with solid-phase sulfur content and dissolution time.
4) Determine the empirical neutralization potentials of solids producing acidic drainage and compare these values to those determined by solid-phase analysis.
5) Determine rates of sulfide and silicate mineral dissolution as a function of dissolution time and drainage pH.

To *summarize the methods*, dissolution tests were conducted on fairly fine ($0.053 < d < 0.149$ mm; $0.18 \leq \%S \leq 1.71$) rock samples that were characterized with respect to chemical composition, mineral content, and mineral chemistry. Tests on ten SKI rock samples (and four Virginia formation samples) from Dunka Mine blast holes were initiated in February 1989 and on four more of these samples in September 1990. These samples were blasted 9 to 64 week prior to experimentation. Dissolution tests on six additional SKI rock samples that had been stored for at least 20 years were initiated subsequently. Some of the tests remain in progress and the following report presents data generated through week 1252. Leached rock samples from terminated tests were examined for dissolution features. This report summarizes drainage quality results, categorizes samples based on sulfur content and minimum drainage pH, and estimates dissolution rates for pyrrhotite, plagioclase, augite, olivine, hypersthene, and biotite.

Dependence of drainage quality on sulfur content of the rock and time was assessed based on dissolution test results. These results indicated that, in general, drainage pH tended to decrease and release rates of heavy metals (copper, nickel, cobalt, zinc) and major cations (calcium, magnesium, sodium, potassium) tended to increase with increasing sulfur content. Based on this observation, samples were divided into three groups based on sulfur content and corresponding drainage quality: Group I, 0.18, 0.22 %S; Group II, $0.40 \leq \%S \leq 0.70$; and Group III, $0.70 < \%S \leq 1.64$. Drainage pH for the Group I samples was generally above 6.0. The minimum drainage pH values for Groups II and III were 3.8 and 3.0, respectively. Minimum pH values and corresponding maximum sulfate release values were typically

attained after 300 to 400 weeks (6 to 8 years) of dissolution. The maximum time to minimum pH was roughly 800 weeks, emphasizing the fact that short term drainage quality results do not necessarily reflect long-term trends. The decreasing sulfate release following attainment of maximum values was attributed to development of coatings on the sulfide mineral surface, and this was supported by photographs of leached sulfide grains. Diminishing sulfide mineral content over time contributed, to a lesser extent, to the decrease in sulfate release.

Neutralization potentials (NP) are a measure of the capacity of a sample to neutralize acid, and this capacity was determined empirically based on the drainage quality observed in dissolution tests. The empirical neutralization potential (ENP) was used for comparison with results from three methods used to determine NP based on solid-phase analysis. ENP values typically fell between 0.5 and 2 kg $CaCO_3$/t rock. NP calculated using carbon dioxide analysis to estimate total calcium plus magnesium carbonate content were closest to the ENP values (<0.7 to 2.5 kg $CaCO_3$/t rock), therefore the best estimate of the capacity of these samples to neutralize acid. Values determined on a subset of samples by a direct titration technique (Lapakko 1994a) yielded values roughly 1 to 3 kg $CaCO_3$/t rock higher than the observed values. Values determined by one common method (Sobek et al. 1978) almost always fell between 12 and 21 kg $CaCO_3$/t rock, substantially higher than the observed values. These results indicate that caution must be exercised when selecting solid-phase methods for determining NP and interpreting the results generated.

Mineral dissolution rates were calculated for an iron sulfide mineral and five silicate minerals. The iron sulfide (pyrrhotite) oxidation rates were based on sulfate release and, at circumneutral pH, were in reasonable agreement with rates reported for laboratory tests on pyrrhotite alone (i.e. in the absence of other minerals). These rates were higher under conditions of low pH and tended to increase after 300 to 400 weeks of dissolution, following a period of low pH and high sulfate release. Silicate dissolution rates calculated using four different models were generally in fair agreement. There did not appear to be strong dependence of rates on pH, with the exception of augite dissolution rates, and generally little dependence on time of dissolution. These estimates are intended to facilitate extrapolation of results from the rock samples examined to rock of varying mineral content within the Duluth Complex.

In summary these results demonstrate the 1) dependence of sulfide mineral oxidation (as reflected by sulfate release) and the attendant acid production on the amount of sulfide minerals present; 2) importance of sulfide mineral oxidation as a driving force for release of sulfate, acid, heavy metals and major cations; 3) importance of long-term dissolution tests in obtaining a technically defensible empirical foundation for mine waste drainage quality prediction; 4) caution that must be exercised when assessing the capacity of rock to neutralize acid based on solid-phase analyses; and 5) potential for determining mineral dissolution rates from laboratory test results and thereby extrapolating results to variable compositions of Duluth Complex rock.

Practical implications of these results for environmentally sound management of waste rock generated by mining in Minnesota include the potential for managing waste rock based on sulfur content, a relatively simple analytical assessment. Based on drainage pH alone, disposal of waste rock in Group I (%S ≤ 0.22 %) would probably require no rigorous reclamation. Potential impacts of sulfate, copper, nickel, cobalt, and zinc release from rock in this range of sulfur content would require consideration. In order to meet water quality standards, waste rock producing drainage pH values similar to Group III samples (0.70 < %S ≤1.64) would require the most rigorous control measures of the samples tested. Elevated release of sulfate and heavy metals from these groups would likely require mitigation as well. The results have implications of substance to mine waste drainage quality prediction. First, caution that must be exercised when assessing the capacity of rock to neutralize acid based on solid-phase analyses designed to quantify NP. Second, results generated from short-term dissolution tests do not necessarily

simulate long-term drainage quality. Emphasizing this point, drainage pH from one sample was circumneutral for 800 weeks and then acidified, reaching a minimum pH of 3.8. Third, tests conducted on samples that had been stored for 8 to 20 years yielded lower rates of sulfate release and higher drainage than samples within about one year of excavation. Therefore, samples used for mine waste drainage quality prediction should be tested as close to the time of their excavation as possible.

Additional work should be conducted to further the benefits generated to date. This includes continued dissolution testing to confidently define long-term trends, analysis of leached solids to increase understanding of chemical reactions controlling solute release (e.g. chemical precipitation and adsorption), and more detailed analysis of the present data, including calculation of mineral dissolution rates. Furthermore, the methods for calculating mineral dissolution rates and approaches for other aspects of data analysis developed for this project should be applied to experiments examining dissolution of Partridge River Intrusion rocks.