THE JAROSITE GROUP OF COMPOUNDS –

STABILITY, DECOMPOSITION AND CONVERSION

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I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Graham Andrew Reynolds.

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Abstract

The jarosite group of compounds are yellow/brown clay like substances, both naturally occurring and synthetically produced in metallurgical processes. Jarosites have the structure $MFe_3(SO_4)_2(OH)_6$, where M can be numerous elements or compounds, most often potassium or sodium. The term jarosite refers specifically to the potassium form of the compound, but is synonymous with the whole group of compounds, often leading to confusion.

In nature, jarosites can be associated with acid mine drainage and acid sulphate soils as an intermediate product of the oxidation of pyrite and other iron/sulphur bearing minerals. In industry, jarosites are used in metallurgical processes, synthetically produced to precipitate an easily filterable form of solid iron. Jarosites have properties that make them a chemically unstable solid. Upon decomposition the jarosite group of compounds will generate sulphuric acid.

A literature review found many references to jarosites, their stability, methods of conversion to iron oxides, methods to extract reusable materials and environmental concerns. Most methods of recycling were unsuccessful. Accelerated conversion of jarosites to a form of iron oxide was a successful method of mitigating the risk of future acid generation. There were numerous specific ways of completing this task.

The BHP Billiton patented nickel atmospheric leach process generates natrojarosite (sodium form of the compound) as a by-product, when extracting nickel from lateritic ores. The by-product of this process was tested for stability to understand the decomposition process.

Accelerated decomposition of natrojarosite was attempted using limestone and hydrated lime at $90^{O}C$. Limestone did not react with the natrojarosite. Hydrated lime caused extensive dissolution of sodium and sulphur from the solid. However XRD analysis still reported natrojarosite as the solid material, suggesting incomplete decomposition and the formation an amorphous form of iron oxide not detected by XRD. Further decomposition tests were completed

using elevated temperatures and pressures in an autoclave. Natrojarosite was not detectable in the solid phase after treatment at a temperature of 212^{O}C, converting to haematite at temperature above 150^{O}C.

The stability of natrojarosite was measured using a number of methods on two natrojarosite samples sourced from the atmospheric leach process. The methods used were batch agitation, column testing and permeability testing. The aim was to provide a holistic result for the stability of natrojarosite if stored in a waste facility. Results obtained were compared against the standard TCLP test and found to be a more accurate method for measuring the stability of natrojarosite. The tests are more time consuming than TCLP testing but showed that natrojarosite was capable of decomposing to form sulphuric acid with time. This result was not obtained from TCLP tests, which suggested the solid material was stable. It was also found that salt water stabilised natrojarosite. Decomposition occurred in 40 and 80 days respectively, for two natrojarosite samples tested in deionised water. There was no evidence of decomposition after 150 and 280 days respectively for the same two samples. The common ion theory is thought to stabilise the natrojarosite which decomposes in an equilibrium reaction. Excess ions present in solution decrease the propensity for the solid to decompose.

The two natrojarosite samples tested varied in calcium concentration. Limestone and hydrated lime were added to the natrojarosite during the nickel extraction process. Gypsum is theorised to form an impermeable layer around the natrojarosite, increasing the stability of the compound. Gypsum is sourced from the neutralisation reaction between limestone or hydrated lime and the acid generated from natrojarosite decomposition.