Purification process for battery grade manganese sulphate

Wensheng Zhang¹, Li Zeng², Yoko Pranolo³ and Keith R. Barnard⁴

- 1. Principal Research Scientist, CSIRO Mineral Resources, PO Box 7229, Karawara, WA 6152, Australia. Email: <u>wensheng.zhang@csiro.au</u>
- 2. Research Scientist, CSIRO Mineral Resources, PO Box 7229, Karawara, WA 6152, Australia. Email: <u>li.zeng@csiro.au</u>
- 3. Research Technician, CSIRO Mineral Resources, PO Box 7229, Karawara, WA 6152, Australia. Email: <u>yoko.pranolo@csiro.au</u>
- 4. Group Leader Hydrometallurgy, CSIRO Mineral Resources, PO Box 7229, Karawara, WA 6152, Australia. Email: <u>keith.barnard@csiro.au</u>
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ABSTRACT

High purity manganese sulphate monohydrate (HPMSM) is a critical precursor material for the synthesis of various lithium battery cathodes for improved stability, safety, and energy density and reduced material costs. Conventional routes for the production of HPMSM via electrolytic manganese metal (EMM), high purity EMM (HPEMM) or electrolytic manganese dioxide (EMD) are energy intensive, while the direct routes from manganese ores require the challenging separation of manganese from calcium and magnesium in the leach solutions.

The current methods for manganese purification practised in China (a major producer of HPMSM) include highly toxic, polluting fluoride precipitation, solubility-based crystallisation with low selectivity and efficiency, and direct solvent extraction (SX). Various SX extractants and synergistic SX (SSX) systems have been studied; however, all of the SX processes suffer from one or more issues including: use of expensive organic reagents, low loading capacity, efficiency and selectivity, high solubility of organic extractants in aqueous solution and thus loss of extractant, and chemical instability of some synergist reagents in the SX process making them unsuitable for commercial applications.

In response to the need for a simple and robust SX process suitable for generating high purity manganese products, CSIRO has recently developed a novel SX process using a non-expensive, non-synergistic reagent system arranged in a simple extract-scrub-strip configuration with a small number of stages at practical organic to aqueous (O/A) volume ratios. The process, which features high loading capacity, high selectivity and high throughput, is suitable for the purification of various leach solutions containing high concentrations of manganese, calcium and magnesium. This CSIRO-developed system has been demonstrated at laboratory scale to produce nearly saturated manganese sulphate liquor containing little or no Ca, Mg, Na/K/NH₄⁺. Such a solution will require little or no evaporation for production of HPMSM, ultrahigh purity manganese sulphate (UPMSM) or greater than 99.99% purity products.