

**Mineralogical and Geochemical Characterisation of Phosphogypsum Waste  
Material and its Potential for use as Backfill at WMC Fertilizers' Mine Site,  
Phosphate Hill, N-W Queensland.**

**Thesis submitted by  
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in May 2004**



**Plate 1.1. Fertilizer production facility, Phosphate Hill, November 2000**

**for the degree of Master of Science (Research)  
in the School of Earth Sciences  
James Cook University.**

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## *Abstract*

The WMC Fertilizers operation at Phosphate Hill, north-west Queensland, began production of ammonium phosphate fertilizer in late 1999. In the production process, Cambrian marine phosphorites are crushed and dissolved (acidulated) in sulphuric and phosphoric acid to produce stronger phosphoric acid and, as a by-product, phosphogypsum (PG). The phosphoric acid is used, with ammonia, for fertilizer production while the PG is permanently stored on-site in gypsum stacking facilities.

In common with other fertilizer plants, the volume of PG in storage at Phosphate Hill has increased rapidly. Eventually tens of millions of tonnes of the material will need to be maintained in permanent facilities. Above-ground stacks, such as those currently used, will be subject to erosion, potentially forming sources of pollutants for the surrounding pastoral country. An alternative option is to store the PG in the voids left after mining of the phosphorite ore body. This would immediately negate most opportunities for erosion of, and contamination from, the storage facilities. This study was instigated to assess the likely impact of in-pit disposal.

Very little work had been done on characterizing the PG produced at Phosphate Hill. A single initial set of analyses taken from samples obtained during the commissioning period identified the major components and subjected the material to rigorous mechanical testing. By contrast, this study has focussed on fully identifying the mineralogy, chemistry, radiochemistry and physical characteristics of the PG in its two main species: the hemihydrate (bassanite -  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) as it is produced from the phosphoric acid plant and the dihydrate (gypsum -  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) that is transported from the re-slurry tank into the gypsum stack for storage. In addition, the liquid component of the PG slurry, derived from acid process water that is recirculated through the stacking system, has also been analysed.

The results show that the four species of calcium sulphate can be found in the PG. Bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) is dominant in the hemihydrate filter cake but also remains in the stack material. Dihydrate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), including species with extra

H<sub>2</sub>O molecules (identified as \*.0.5H<sub>2</sub>O), dominates the stack gypsum but also occurs at low levels in the hemihydrate filter cake. Anhydrite (CaSO<sub>4</sub>) is also found at low levels within samples from both areas.

Quartz (SiO<sub>2</sub>) is the other dominant mineral in the PG assemblage. This is at significant levels (>20%) and causes the PG to be notably different to that produced elsewhere in the world, where quartz makes up <1% of the total. The high volumes of this mineral result from the make-up of the parent phosphorite ore body, which has a comparatively high level of chert and silicified siltstone and shale.

P<sub>2</sub>O<sub>5</sub> levels are elevated and relate primarily to the presence of co-precipitated and re-precipitated phosphates and remnant phosphoric acid with very minor amounts of unreacted phosphorite and phosphatised chert and siltstone. Mica (paragonite [NaAl<sub>2</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>] and probably muscovite [K<sub>2</sub>Al<sub>4</sub>[Si<sub>6</sub>Al<sub>2</sub>O<sub>20</sub>](OH,F)<sub>4</sub>] and glauconite [(K,Ca,Na)<sub>-1.6</sub>(Fe<sup>3+</sup>,Al,Mg,Fe<sup>2+</sup>)<sub>4.0</sub>Si<sub>7.3</sub>Al<sub>0.7</sub>O<sub>20</sub>(OH)<sub>4</sub>] sourced from the ore body) was a consistent presence at low levels in the PG mix. An unidentified amphibole was also found, although some doubts exist as to the accuracy of the XRD technique to adequately identify such minerals at the low levels seen here. If correct, the latter is probably from the hornblende group (magnesiohastingsite to hastingsite) that occurs in the basement Kalkadoon Granodiorite, or from the basement Proterozoic metasediments of the Plum Mountain Gneiss and Corella Formation. Various clays, most commonly smectite ((1/2Ca,Na)<sub>0.7</sub>(Al,Mg,Fe)<sub>4</sub>[(Si,Al)<sub>8</sub>O<sub>20</sub>](OH)<sub>4</sub>.nH<sub>2</sub>O) and clinoptilolite ((Na,K)<sub>6</sub>[Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>].24H<sub>2</sub>O) were also consistently present.

Major element analyses are consistent with the mineralogical interpretation. Elements, apart from Ca, S and Si and including F, were at levels similar to those found in PG manufactured at other sites around the globe. Trace elements showed elevated levels of Ba, Mn and Pb relative to foreign-sourced PG. This appears to reflect the primary and secondary (weathering products) mineralogy of the ore body.

Crystal morphology was also shown to be similar to that produced abroad, at sites as diverse as the USA, north Africa and the Middle East. The gypsum component of the Phosphate Hill PG appears to contain fewer acicular crystals and no swallow-tail twins were observed, unlike at other sites. Massive clusters are common.

Radiochemical analyses have identified U-238, Po-210, Pb-210, Ra-226 and Rn-222 as being present in the ore and throughout the manufacturing process. All are present to varying degrees in the PG but the U-238 tends to partition more into the fertilizer. None of the radionuclides occur at levels that could be considered a risk. However, the study has identified that recirculation of the fluids through the re-slurry-stacking circuit is concentrating the radionuclides occurring in the process water. This issue will need to be monitored and addressed by the Company in future.

The second part of the project has been to study the effects of dissolution on the PG if placed into surface mining voids as backfill. At Phosphate Hill, potential dissolution of mine backfill material can be derived from two sources. The first is the monsoonal “wet season” over summer, where individual rain events can result in over 150mm of rain falling in the space of a few hours, leading to flash flooding and inundation of wide areas around the local watercourses. This has the potential to result in the temporary submergence of any of the backfilled areas located within the flood plain. The second source is from interaction of the PG with the groundwater. The latter will occur because the Beetle Creek Formation, which hosts the ore body, also contains the local aquifer and post-mining recharge will see the SWL return to pre-mining levels, well above the floors of the pits.

Dissolution experiments were performed using hemihydrate and two forms of dihydrate PG, simulating approximately two years’ annual rainfall/intermittent full inundation of a PG backfill pile by either groundwater or floodwater. The dihydrate PG was newly-deposited material that still contained high levels of fluid and “aged” dihydrate that had been on the stack for 4-6 months and was dry. Analyses of the dissolution and the pre- and post-dissolution PG showed that highly contaminated dissolution would occur in the first 2-3 flushing events and that levels of contaminants fall rapidly with further flushing. The major long-term contaminant has been identified as sulphates and acid derived from gypsum dissolution. Ca and total P are also significant. Radionuclide analysis of leachate could not be undertaken in this study but should be considered for any future studies, if the Company plans to utilise in-pit disposal of PG.

Gypsum dissolution is also likely to be a long-term problem in that the aquifer is essentially a closed system. This, along with the dominant flow direction, will result in concentration of any contaminants in the southern part of the aquifer. Basic simple modelling of the effects of a sulphate-rich solution mixing with the groundwater at its current quality suggests that the sulphate may reach levels of concern for human consumption (*i.e.* >500mg/l) with an input of contaminated fluid the equivalent of <25% of the total volume of the aquifer. As the site is covered by active pastoral leases the effect of sulphate contamination of groundwater on cattle was also considered. In this environment problems occur at sulphate levels of ~1000mg/l which the modelling suggests would not occur until a mix of 50% leachate to 50% groundwater was achieved. Although this appears to be a remote possibility for contamination of the whole aquifer, the very high transmissivity of the aquifer will result in a polluted plume being drawn directly into wells that are pumping, which could easily result in the ingestion of poor quality water by cattle drinking from troughs supplied by any such bore. Acidification of the groundwater could also possibly occur with the escape of acid leachate into the aquifer, with the pH of the water rapidly falling below the preferred minimum of pH 6 at relatively low levels of mixing (10% leachate to 90% groundwater). Acidification to this extent can cause acidosis in cattle, a condition that is potentially fatal.

Phosphorous is also present in high levels in the PG leachate. There is potential for this to lead to outbreaks of toxic cyanobacteria in water storage tanks and troughs in the warmer months, which can result in fatalities in cattle through liver or respiratory failure. However, this potential may be buffered by the likely acidity of any high-P leachate, as cyanobacteria prefers neutral to alkaline water conditions.

Although contaminated leachate can be largely contained by use of liners and capping material, the use of PG as backfill at Phosphate Hill faces challenges that would be extremely difficult to overcome. The mining method leaves walls that are sub-vertical (>70°) and exposes the full ore seam on the down-dip side of the ore body. Pit floors have a dome-and-basin morphology. Although the latter could be flattened and lined, the steep walls, with their exposures of abrasive, sharp-edged phosphorite would preclude the use of most lining materials. The scale of earth-moving and lining required would also be cost-prohibitive.



The type of PG used for backfilling operations and the method of delivery also create difficulties. Filter cake hemihydrate PG would require a very large truck fleet and/or the construction of a new overland conveyor. Once deposited, the material's tendency to form large, loose clumps would allow rapid through-flow of fluids. PG slurry could be piped directly to its deposition point, requiring the construction of an extensive pipe network, but is otherwise completely unsuitable for the task due to the liquid component. Dry dihydrate PG is the best material for backfill. However, it would also require a very large truck fleet and the act of rehandling the material from stack to pit would create dust problems for the term of the rehandling exercise. After deposition the leachate problem would still exist, albeit produced at a slower rate due to the dihydrate's lower permeability. The leachate problem could be countered by using a layer-cake style of construction where calcareous rocks are interlayered with PG to neutralise any fluids derived from the PG. Despite this, other engineering and environmental issues probably preclude the use of even this method of backfill.

This study has produced the base-line information required for any future work involving the PG, such as the recommendation for trials of in-pit dumping to go ahead, observing a range of conditions. As a result, it is recommended that WMCF only use dihydrate PG as backfill in areas that are well above the natural standing water level and that have been adequately lined. The majority of PG will still need to be stored in lined and capped stacks, as are currently used. It is also recommended that the radionuclide content of the recycled stack fluids being regularly monitored and plans drawn up to deal with the contaminated fluids if it proves necessary. Future research should also be conducted on radionuclide transport and behaviour in PG leachate.

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## Abbreviations

|       |   |
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| ANSTO | Australian Nuclear Science and Technology Organisation      |
| DH    | Dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )     |
| FRP   | Filterable reactive phosphorous                             |
| GSF   | Gypsum storage facility                                     |
| HH    | Hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) |
| JCU   | James Cook University                                       |
| ICPMS | Inductively coupled plasma mass spectrometry                |
| NMR   | Nuclear magnetic resonance                                  |
| PAP   | Phosphoric acid plant                                       |
| PG    | Phosphogypsum   |
| SEM   | Scanning electron microscopy                                |
| SWL   | Standing water level  |
| TEM   | Transient-domain electromagnetics                           |
| WMCF  | WMC Fertilizers   |
| XRD   | X-ray diffraction   |
| XRF   | X-ray fluorescence  |