

**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
Susan Katherine DIPPEL BSc (Hons) NSW
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.**

STATEMENT OF ACCESS

I, the undersigned, the author of this thesis, understand that James Cook University will make it available for use within the University Library and, via the Australian Digital Theses network, for use elsewhere.

I understand that, as an unpublished work, a thesis has significant protection under the Copyright Act and I do not wish to place any further restriction on access to this work.

Signature

Date:

STATEMENT OF SOURCES

DECLARATION

I declare that my thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

Signature

Date

Acknowledgements

WMC Fertilizers and WMC Resources for providing the research project and funding/study time to support it. The staff of the Mining and Gypsum department for assistance, support and encouragement at all times during the project. James Cook University for supporting the project by providing a scholarship covering HECS.

Mr Shane Barker, Mr Jeremy King, Mr Adrian Royal, Mr Nick Supljaglev and the gypsum crew for very helpful advice, suggestions and general assistance in the sampling and interpretation operations. Mr Craig Ritchie for discussions and practical assistance on chemistry-related matters. Mr Bruce Sommerville for discussions on the intricacies of correlation coefficients and other matters statistical and for production of ore body averages. Mr Fortunato Rossi and FlightWest, Ansett and Alliance Airlines at various times for permission to transport the samples by air from site to Townsville.

My supervisor, Assoc Prof Bernd Lottermoser, for his guidance and assistance (scientific and editorial) throughout the course of the project. Mr Paul Givney of the Department of Earth Sciences, James Cook University, Townsville Campus, for construction of the dissolution columns. Ms Michelle Hough, PhD student at JCU, Townsville, for discussions on phosphorites and for generously allowing me use of some of her material.

Mr Alan Chappell, Dr Kevin Blake and staff at the Advanced Analytical Laboratories of JCU for prompt analyses and helpful advice. Mr John Faithful and staff at the Australian Centre for Tropical Freshwater Research at JCU for analyses of leachate. Dr Sue Brown and staff of the Australian Nuclear Science and Technology Organisation for efficient radionuclide analyses and discussions. Mr Doug Abbott of SNF (Australia) Pty Limited for clarification of Phosphate Hill flocculants. The Florida Institute of Phosphate Research library for promptly providing reams of background research material on phosphogypsum.

Most importantly, my husband, Perry, for general support, encouragement and the occasional bit of pushing to get things done.

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

H₂O molecules (identified as *.0.5H₂O), dominates the stack gypsum but also occurs at low levels in the hemihydrate filter cake. Anhydrite (CaSO₄) is also found at low levels within samples from both areas.

Quartz (SiO₂) 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.

P₂O₅ 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 [NaAl₂(Si₃Al)O₁₀(OH)₂] and probably muscovite [K₂Al₄[Si₆Al₂O₂₀](OH,F)₄] and glauconite [(K,Ca,Na)_{-1.6}(Fe³⁺,Al,Mg,Fe²⁺)_{4.0}Si_{7.3}Al_{0.7}O₂₀(OH)₄] 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)_{0.7}(Al,Mg,Fe)₄[(Si,Al)₈O₂₀](OH)₄.nH₂O) and clinoptilolite ((Na,K)₆[Al₆Si₃₀O₇₂].24H₂O) 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.

Table Of Contents

1.0	INTRODUCTION	2
1.1	Purpose	3
1.1.1	Previous Work	3
1.1.2	PG Production	4
1.1.3	PG Research	5
1.1.4	Limitations on PG Re-use	8
1.2	Location	9
2.0	BACKGROUND	12
2.1	Introduction	13
2.2	PG Stacking	13
2.3	Geology	14
2.3.1	Regional Setting	14
2.3.2	Duchess Embayment	18
2.3.3	Ore Body – Monastery Creek Phosphorite Member	22
2.4	Hydrogeology	28
2.5	Production Process Overview	32
2.5.1	Mining Method and Stockpile Management	32
2.5.2	Beneficiation Plant	35
2.5.3	Phosphoric Acid Production	36
2.5.4	Ammonia and Granulation Plants	40
2.5.5	Sulphuric Acid Plant	43
2.5.6	PG Stacking Method	45
3.0	METHODOLOGY	51
3.1	Introduction	52
3.2	PG Slurry Sampling	53
3.2.1	Equipment	55
3.2.2	Method	56
3.3	Dihydrate Sampling	57
3.4	Hemihydrate Sampling	57
3.5	Dissolution Column Analyte Sampling	58
3.5.1	Field Leach Columns	58
3.5.1.1	Equipment	58

3.5.1.2 Method	60
3.5.2 Laboratory Dissolution Columns	61
3.5.2.1 Equipment	62
3.5.2.2 Method	63
3.6 Methods of Analysis	64
3.6.1 X-Ray Fluorescence Spectrometry(XRF)	65
3.6.1.1 Semi-quantitative X-ray Fluorescence Spectrometry	65
3.6.1.2 Quantitative X-ray Fluorescence Spectrometry	65
3.6.2 Powder X-Ray Diffraction (XRD)	66
3.6.3 Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Atomic Spectrometry (ICPAES)	67
3.6.4 Particle Sizing	67
3.6.5 Scanning Electron Microscope (SEM)	68
3.6.6 Analyte Chemistry	68
3.6.7 Radionuclides	68
3.7 Sampling Objectives	69
4.0 RESULTS	71
4.1 Introduction	72
4.2 PG Slurry	72
4.2.1 PG Slurry Liquid Phase Chemistry	74
4.2.2 PG Slurry Solid Phase (Dihydrate) Chemistry	77
4.2.3 Relative Elemental Abundance	80
4.2.4 PG Particle Slurry Sizing	81
4.2.5 Seasonal Variation	82
4.2.6 Heavy Metals	88
4.3 Dihydrate PG	90
4.3.1 Dihydrate PG XRF Results	91
4.3.2 Dihydrate PG SEM Results	93
4.3.3 Correlation Coefficients	96
4.4 Hemihydrate PG	98
4.4.1 Hemihydrate PG XRF Results	98
4.4.2 Hemihydrate PG SEM Results	100

4.5	Non-PG phases	101
4.6	Dissolution Columns	105
4.6.1	Pre-Dissolution PG Analyses	105
4.6.2	Post-Dissolution PG Analyses	107
4.6.3	Analyte Leachate Results	115
4.6.4	Physical Response of PG to Addition of Water	121
4.6.4.1	Hemihydrate PG	122
4.6.4.1(i)	Age	122
4.6.4.1(ii)	Particle Size	123
4.6.4.1(iii)	Dissolution Behaviour	123
4.6.4.1(iv)	Particle Growth	123
4.6.4.1(v)	Water Retention	123
4.6.4.2	“New” Dihydrate PG	124
4.6.4.2(i)	Age	124
4.6.4.2(ii)	Particle Size	124
4.6.4.2(iii)	Dissolution Behaviour	125
4.6.4.2(iv)	Particle Growth	125
4.6.4.2(v)	Water Retention	126
4.6.4.3	“Old” Dihydrate PG	126
4.6.4.3(i)	Age	126
4.6.4.3(ii)	Particle Size	126
4.6.4.3(iii)	Dissolution Behaviour	126
4.6.4.3(iv)	Particle Growth	127
4.6.4.3(v)	Water Retention	127
4.7	Radionuclides	127
4.8	Summary	129
5.0	DISCUSSION	131
5.1	Introduction	132
5.2	Chemical and Physical Characteristics of PG	133
5.3	Slurry Liquid	150
5.4	Element Abundance in PG Slurry	151
5.5	Particle Sizing	153
5.6	Seasonal Variation Within PG Slurry Solid and Liquid Chemistry	154
5.7	Dissolution Column Results	157

5.8	Radionuclides	161
5.9	Potential for Use of PG as Mine Backfill	163
5.10	Summary	195
6.0	CONCLUSIONS AND RECOMMENDATIONS	197
6.1	Conclusions	198
6.2	Recommendations	205
7.0	BIBLIOGRAPHY	206
8.0	APPENDICES	
Appendix 1.	PG Slurry Sampling Results	223
Appendix 2.	Phosphoric Acid Plant Daily Log Sheets, PG Slurry Sampling	245
Appendix 3.	2003 Sampling Sites For Metals and Radionuclides	294
Appendix 4.	Surveyed PG Stack Growth Rates	296
Appendix 5.	Results of DH PG Leaching Experiments carried out By Environmental Geochemistry International for In-Pit Disposal Trial	300
Appendix 6.	Approximate Pit Void Volumes: Calculations	302
Appendix 7.	Dissolution Columns	307
Appendix 8.	PG Slurry Particle Sizing Results	322
Appendix 9.	PG Microprobe Reports	324
Appendix 10.	XRF Standards and Reproducibility Data	334
Appendix 11.	Independent Analysis of Slurry Sample PG008A Undertaken by Sietronics Pty. Limited, September 2004	336

List of Tables

Table 2.1	Duchess Embayment stratigraphy at Phosphate Hill (after Russell and Trueman 1971)	21
Table 2.2	Diagenetic and weathering paragenesis for the MCPM (from Hough 2003).	26
Table 2.3	Average element analyses, Phosphate Hill DAP and MAP.	43
Table 4.1	Average Quantified Mineralogy, PG slurry. Note: only one sample contained Heulandite. Type chemical formulae taken from Deer <i>et al.</i> 1992. The specification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it. ? Type chemical formulae for the three known mica species (Hough 2004, Mascini 2001)	73
Table 4.2	Summary of results of physical parameters measured in PG slurry (liquid phase). Note: only one turbidity measurement was available for PG011.	74
Table 4.3	Summary of major element results, PG slurry (liquid phase).	75
Table 4.4	Summary of trace element results, PG slurry (liquid phase).	76
Table 4.5	Summary of XRF major results, PG slurry (solid phase).	78
Table 4.6	Summary of trace element results, PG slurry (solid phase).	79
Table 4.7	Summary of average PG particle sizing results (sizes in microns). n = 24.	82
Table 4.8	Summary of major element results, DH PG.	91
Table 4.9	Summary of trace element results, DH PG.	92
Table 4.10	Summary of average quantified mineralogy, DH PG. *The specification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it.	92
Table 4.11	Correlation coefficients for PG slurry solids – all elements.	97
Table 4.12	Major elements, HH PG (n = 1)	98
Table 4.13	Trace elements, HH PG (n = 1)	99
Table 4.14.	Quantified mineralogy, HH PG. *The specification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it. (n = 1)	99
Table 4.15	Pre-dissolution major element analyses (XRF).	105
Table 4.16	Pre-dissolution minor element analyses (XRF).	106
Table 4.17	Pre-dissolution quantified mineralogy. The specification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it.	106
Table 4.18	Post-dissolution major element analyses (XRF).	107
Table 4.19	Post-dissolution minor element analyses (XRF).	108
Table 4.20	Post-dissolution quantified mineralogy. *The specification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 0.5\text{H}_2\text{O}$ is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it.	108

Table 4.21.	Quantified mineralogy changes, from the pre- to the post-dissolution stage, for new and old DH and HH columns. *This result is almost certainly wrong, probably due to mis-identification of the gypsum species.	111
Table 4.22.	Major element changes, from the pre- to the post-dissolution stage, for new and old DH and HH columns.	112
Table 4.23.	Water retention rates of PG columns	122
Table 5.1.	Characteristics of natural gypsum, average global PG and Phosphate Hill PG (partly derived from Ardaman 2000, Faure 1998, Rutherford <i>et al.</i> 1994, Deer <i>et al.</i> 1992). *Mica includes identified species muscovite, glauconite and paragonite (refer Section 4). ? Undigested phosphorite is due to the self-limiting reaction between apatite and H ₂ SO ₄ which leaves phosphorite particles coated in gypsum.	134
Table 5.2.	Typical major element composition (%) for Florida DH and HH, Iraqi DH, other Australian DH PG and Phosphate Hill HH and DH (average XRF results from this study), compared to natural gypsum. (partly adapted from Khalil <i>et al.</i> 1990, Kouloheris 1980, and Beretka 1980. Note: none of these papers specify the analytical technique used).	135
Table 5.3.	Some examples of average sedimentary phosphorite chemistry (after Abed and Amireh 1999; Becker 1989; Deshmukh 1978; EFMA 2000; Flicoteaux and Lucas 1984; Ilyin and Ratnikova 1981; Lucas and Prevot 1981; McLellan <i>et al.</i> 1985a; McLellan <i>et al.</i> 1985b; Nathan 1984; Sommerville 2003b; Wurzbarger 1968; Yang and Guo 2000). Phosphate Hill averages derived from the Phosphate Hill drilling database as at February 2004 (lithium metaborate analytical technique). ❖Fluoride derived from samples of rock filter cake entering Reactor 1A and analysed internally using ICP.	137
Table 5.4.	Trace elements in PG (ppm) produced from different rock phosphate sources (after Rutherford <i>et al.</i> 1994) compared to Phosphate Hill PG from this study.	146
Table 5.5.	Comparison of sample PG011 with average slurry, leach column and total DH XRF analyses (%). *All DH excludes PG011.	149
Table 5.6.	Comparison of quantified mineralogy for sample PG011 with average slurry, leach column and total DH XRD analyses (%). *The specification of CaSO ₄ .2H ₂ O+*.0.5H ₂ O is the total of standard dihydrate gypsum plus dihydrate with additional partial or complete molecules of water attached to it. ❖All DH excludes PG011.	150
Table 5.7.	Uranium Analyses, Phosphate Hill and Foreign Ore (Brown <i>et al.</i> 2000, Becker 1989)	162
Table 5.8	Average water chemistry, Duchess Embayment Aquifer.	173
Table 5.9	Average water chemistry, Ordovician calcareous sediments. NB: all major and trace element results are from filtered samples.	174
Table 5.10	Modelled (simple mixing) effects of leachate contamination within the Duchess Embayment Aquifer, including major elements.	180

Table 5.11	Modelled (simple mixing) effects of leachate contamination within the Duchess Embayment Aquifer, secondary elements. All measurement in mg/litre.	180
Table 5.12	Guidelines for Livestock Drinking Water – Trigger Values (adapted from ANZECC 2000)	183
Table 5.13.	Changes to pH as a result of leachate/groundwater mixing using logarithms.	184

List of Figures

Figure 1.1	Location of Phosphate Hill (from Passmore and Berry 2002).	9
Figure 1.2	Graph of monthly rainfall in the Phosphate Hill area, 1975-2003. The cyclical nature of the seasons (wet and dry) is evident.	10
Figure 2.1	Regional setting of the Georgina Basin (from Hough 2003). The area shown on figure 2.2 is that outlined above in red	15
Figure 2.2	Regional geological setting for the eastern phosphogenic deposits of the Georgina Basin (after Rogers and Keevers 1976)	16
Figure 2.3	Geological map of the Burke River Outlier showing phosphate deposits (after Russell and Trueman 1971). The railway line now extends to the Phosphate Hill operation from Duchess.	17
Figure 2.4	Geology of the Duchess Embayment (from Rogers and Crase 1979)	19
Figure 2.5	Major structural elements of the Duchess Embayment (from Russell and Trueman 1971)	20
Figure 2.6	Cross-section of exploration trench showing typical mining sequence, Phosphate Hill (north and central zones). Inca Shale (overburden), Monastery Creek Phosphorite Member (ore, divided into 10 units of variable grade) and Lower Siltstone Member (footwall). After Rogers and Crase 1979.	22
Figure 2.7	Stratigraphic Column of the Monastery Creek Phosphorite Member as displayed in Figure 2.6, showing typical grades for P_2O_5 , Fe_2O_3 and Al_2O_3 per Unit.	27
Figure 2.8	Outline of the Duchess Embayment Aquifer (geology after Russell and Trueman 1971). The main body of the aquifer is contained within the siliceous facies of the BCF outlined in purple.	29
Figure 2.9.	Phosphate Hill production bore field as at June 2004. Coloured contours = hanging wall mRL, dashed green line = projected final Galah Pit outline. Black line = approximate position of Mehaffey Creek Fault. North is to the top of the page. Fertilizer plant and slimes dam east of Mehaffey Creek Fault, Galah Pit to the west. Image from Berry <i>pers. comm.</i> 2004.	30
Figure 2.10	Phosphate Hill mining process flow chart (from WMCF Intranet live production pages).	34
Figure 2.11	Phosphate Hill beneficiation plant process flow chart (from WMCF Intranet live production pages).	35
Figure 2.12	Phosphate Hill phosphoric acid plant process flow chart (from WMCF Intranet live production pages).	37
Figure 2.13	Phase diagram controlling gypsum species formation in phosphoric acid plants (from Gobbitt and van Ede 2004).	39
Figure 2.14	Phosphate Hill ammonia plant process flow chart (from WMCF Intranet live production pages). Hot processing side in the upper half of the diagram, cold in the lower half.	40
Figure 2.15	Phosphate Hill granulation plant process flow chart (from WMCF Intranet live production pages)	42
Figure 2.16	Mt Isa sulphuric acid plant process flow chart (from WMCF Intranet live production pages)	44

Figure 2.17	Phosphate Hill PG stack process flow chart (from WMCF Intranet live production pages).	47
Figure 2.18	Schematic of PG wet-stack construction method as used at Phosphate Hill (adapted from Ardaman 1999)	48
Figure 3.1	Schematic of field leach columns (not to scale).	59
Figure 3.2	Actual vs. average monthly rainfall over the field leach column trial period, August 2000 to July 2001.	61
Figure 3.3	Schematic of laboratory leach columns (not to scale).	63
Figure 4.1	Major element relative abundance, PG slurry (ppm). n = 24 for both phases.	80
Figure 4.2	Trace element relative abundance, PG Slurry (ppm). n = 24 for both phases.	81
Figure 4.3	Beneficiation and phosphoric acid plant feed grades at PG slurry sampling dates. Pink = raw rock into beneficiation plant (mean of 3 samples taken over 24 hours on each sampling date); Blue = crushed and washed rock filter cake into PAP reactor 1A (mean of 7 samples over 24 hours on each sampling date). ICP data from WMCF PIMS database	83
Figure 4.4	Quantified mineralogy trends (all gypsum species) over 12 month slurry sampling period. n = 24. Blue is the total of all gypsum species in a given sample; pink is the mean of all samples over the 12 month period; green and brown = +/- two standard deviations of the mean.	84
Figure 4.5	XRF trends for SiO ₂ over 12 month slurry (solids) sampling period. n = 24 Blue = total SiO ₂ in each sample. Pink is the mean of all samples over the 12 month period; green and brown = +/- two standard deviations of the mean.	84
Figure 4.6	Solids content of slurry samples. n = 24	86
Figure 4.7	Comparison of gypsum species (quantitative mineralogy) in slurry over the 12 month sampling period.	87
Figure 4.8	XRF solid phase trends for Pb over 12 month slurry sampling period. n = 24. Blue = ppm Pb in monthly sample; pink = mean of all samples over 12 month sampling period; purple and puce = +/- 1 standard deviation of the mean; green = + 2 standard deviations of the mean.	88
Figure 4.9	ICP liquid phase trends for Pb over 12 month slurry sampling period. n = 24. Blue = Pb in monthly sample; pink = mean of all samples over 12 month sampling period; green and brown = +/- 2 standard deviations of the mean.	88
Figure 4.10.	ICP liquid phase trends for Cd over 12 month slurry sampling period. n = 24. Blue = Cd in monthly sample; pink = mean of all samples over 12 month sampling period; green and brown = +/- 2 standard deviations of the mean.	89
Figure 4.11	pH trends (averaged for each month) in PG slurry over 12 month sampling period. n = 24.	90
Figure 4.12.	Energy dispersive spectra examples – bulk of sample (DH).	96
Figure 4.13	Energy dispersive spectra – quartz grains.	96
Figure 4.14	Energy dispersive spectra examples – Cr-Fe grains.	96
Figure 4.15	Pre- and post-dissolution SiO ₂ content (XRF), all columns.	109

Figure 4.16	Pre- and post-dissolution bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) content (XRD), all columns.	109
Figure 4.17	Pre- and post-dissolution DH ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) content (XRD), all columns.	110
Figure 4.18	Pre- and post-dissolution anhydrite (CaSO_4) content (XRD), all columns.	111
Figure 4.19a	Primary major element content (XRF), pre- and post-dissolution, all columns.	112
Figure 4.19b	Secondary major element content (XRF), pre- and post-dissolution, all columns.	113
Figure 4.20a	Primary trace element content (XRF), pre- and post-dissolution, all columns.	114
Figure 4.20b	Secondary trace element content (XRF), pre- and post-dissolution, all columns.	115
Figure 4.21	pH trends in leachate, all columns.	116
Figure 4.22	Conductivity trends in leachate, all columns.	116
Figure 4.23	Phosphorous and silica trends in leachate, all columns.	117
Figure 4.24	Major element trends in leachate, hemihydrate column.	118
Figure 4.25	Major element trends in leachate, freshly-deposited DH column.	118
Figure 4.26	Major element trends in leachate, aged DH column.	119
Figure 4.27	Trace element trends in leachate, HH column.	120
Figure 4.28	Trace element trends in leachate, freshly deposited DH column.	120
Figure 4.29	Trace element trends in leachate, aged DH column.	121
Figure 4.30	Radionuclide trends, PG slurry solid phase.	128
Figure 4.31	Radionuclide trends, PG slurry liquid phase.	128
Figure 5.1	XRD profile of sample PG008A. Sample amphibole peak is between 10 and 11 on the X-axis, SIROQUANT type amphibole peak is in red at 10.5.	141
Figure 5.2	Comparison of major element results (XRF) in Phosphate Hill DH PG. Lilac = mean of all crystalline DH PG sampled; dark red = mean of all slurry solids; cream = mean of all crystalline and slurry solids; green = PG011 solids.	145
Figure 5.3	Moisture retention in PG leach columns.	148
Figure 5.4	PG Particle Size Distribution, average of all slurry samples.	153
Figure 5.5	Trends in CaO, SO_3 , P_2O_5 and F (XRF) in PG solids over 12 month slurry sampling period.	155
Figure 5.6	Phosphoric Acid Plant efficiency chart over slurry sampling period.	155
Figure 5.7	pH vs. EC trends during leaching period for HH and DH PG.	158
Figure 5.8	Example of major element trends during leaching period, HH and DH PG.	158
Figure 5.9	Example of trace element trends, PG leachate.	159
Figure 5.10	Radionuclide trends, PG leachate.	162
Figure 5.11.	Height of gypsum stack phreatic surface <i>versus</i> time (from Kleinschmidt 1990). Recharge rate is the equivalent of 12.7cm/year. The starting point (y-axis) is the equivalent of the highest level expected to be attained by Cell 4 at Phosphate Hill (~70m).	164

Figure 5.12	Current mining voids, Phosphate Hill. The coloured lined represent the modelled SWL drawdown (3-month intervals) at current pumping rates until early 2006. Future mining areas (post 2009) will move into the submerged zone between Brolga and Magpie and north and east of both Corella and Jabiru. A-A ¹ represents the cross-section presented in Figure 5.13. B-B ¹ represents the eastern end of the cross-section presented in Figure 5.17.	171
Figure 5.13	South-North long-section along 93200E (A-A ¹). Larger sampling intervals = 1m, smaller = 0.5m. Any PG used as fill in the final void would be subject to permanent inundation between the blue (final SWL) and brown (final pit floor) lines.	172
Figure 5.14.	WMC risk analysis and ranking tables.	176
Figure 5.15	Cross-sectional representation of the WMCF aquifer numerical model. (From Dippel and Wharton 2003).	181
Figure 5.16.	Illustration of probable solute transport paths defined by PMPATH under the current pumping regime using the WMCF numerical model. Fewer ticks = faster flow.	182
Figure 5.17	Geophysical cross-section, along 78000N, showing the morphology of the thickest part of the DEA and the groundwater's relationship to the BCF (green = top of MCPM, dotted line = base of LSM) and local major structures, lithological and facies changes. B-B ¹ represents the portion of the section shown on Figure 5.12. Base illustration from Golden <i>pers. comm.</i> , 2003, from NMR data obtained during the 2002 aquifer definition program. Geology and structure added by the author from drilling results and mapping. From Dippel and Golden, 2003.	186
Figure 5.18	Calcareous zone (green) within current resource boundary (red) and siliceous aquifer (blue). Current lease in purple, site geography in grey.	191

List of Plates

Plate 1.1	Fertilizer production facility, Phosphate Hill, November 2000	cover
Plate 1.2	Phosphate Hill PG Stack (Cells 1 and 2), October 2000.	1
Plate 1.3	A view of the Phosphate Hill area, looking north towards The Monument and Mt Bruce. North-western slopes of Phosphate Hill in the foreground with black soil plains in the centre and typical low-moderate relief land forms on the horizon.	10
Plate 2.1	Phosphate Hill PG Stack (Cells 1 and 2) and Re-slurry tank, March 2001.	12
Plate 2.2	Weathered, siliceous MCPM, Galah pit, Phosphate Hill mine. Dashed blue lines separate Units 3, 4 and 5. Note the increased volume of siltstone and shale in lower grade Units 3 and 5 compared to almost pure phosphorite in Unit 4. Ch = chert, IP = indurated phosphorite, FP = friable phosphorite, SS = siltstone, Sh = shale.	23
Plate 2.3	Thin section of phosphate peloids with iron hydroxide (Fe) contaminants and chert (Ch), plane polarised light (from Hough 2003)	24
Plate 2.4	Thin section of collophane mudstone bed with radial features from possible microbial action (from Hough 2003).	25
Plate 2.5	Glauconitisation in apatite peloid (from Hough 2003). Fe = iron hydroxide inclusions within the apatite peloid. Gl = glauconite; Ap = Apatite.	25
Plate 2.6	Footwall cleanup, Galah pit parcel 602, September 2003. The 200 tonne excavator peels the ore (grey MCPM) from the footwall (yellow LSM), following the contours of the contact. Also visible in the background is the Inca Shale overburden.	29
Plate 2.7	Partially recovered ROM stockpile 2. 4.5 lifts are visible with a fifth obscured behind the rill at the base of the stockpile. Individual truck dumps that have been flattened by a bulldozer are also visible (brown lines). Stockpile construction is orthogonal to this face. Ore affected by iron hydroxide alteration appears as orange in the upper lifts.	30
Plate 2.8	Phosphate Hill beneficiation plant, looking east from the rail loadout hopper towards Galah North pit. The three slurry holding tanks are off the photo to the right. PJC = primary jaw crusher, SCC = secondary cone crusher, TCC = tertiary cone crusher and drum scrubber, BM = ball mill.	36
Plate 2.9	Phosphate Hill PAP looking north over beneficiation tertiary crusher. RFB = rock slurry filtration belts, ART = acid reactor tanks, GFF = gypsum filter belt floors, AST = acid storage tanks.	38
Plate 2.10	Phosphate Hill ammonia plant.	41
Plate 2.11	Granulation plant and storage shed, Phosphate Hill.	42

Plate 2.12.	Mt Isa sulphuric acid plant (centre) with Xstrata copper smelter to the right. Acid storage tanks and rail load-out facility on the left.	45
Plate 2.13	Hemihydrate PG and acid process water being mixed in the re-slurry tank. The black substance floating on the top is believed to be of organic origin.	46
Plate 2.14	Long-arm excavator building rim ditch, Cell 1, October 2000. Cell 2 is visible directly behind the excavator and the return surge ditch is visible to the left.	49
Plate 3.1	Phosphate Hill PG Stack (Cells 1 and 2) and Re-slurry Tank, April 2002	51
Plate 3.2	Re-slurry tank and launder discharging into Cell 1, October 2000.	54
Plate 3.3	Initial sample point: PG slurry discharging from the end of the launder directly into the rim ditch.	54
Plate 3.4	Sampling point: spigot discharging PG slurry into rim ditch.	55
Plate 3.5	Sampling point: HH PG being discharged from overland conveyor into re-slurry tank.	57
Plate 3.6	Field leach columns in place, Galah North pit.	60
Plate 4.1	Phosphate Hill PG Stack (Cells 1 and 2) and Re-slurry Tank. Stack completed, September 2003	71
Plate 4.2.	(Left) Secondary electron image of typical DH PG morphology; (right) Backscatter electron image of DH PG which shows very little variation in the average chemistry of the grains (freshly deposited DH sampled from top of stack)	94
Plate 4.3.	Backscatter electron image of large quartz grain (B – dark grey) with gypsum (A – mid grey) and Cr-Fe grains (C - white).	94
Plate 4.4.	(Left) Secondary electron image of DH PG cluster containing angular quartz grains (F), fine gypsum+phosphorous+quartz (E) and bulk gypsum (D) and (Right) large angular quartz clasts (F) with matrix gypsum (D) (approximately 6-months old DH sampled from within the stack).	95
Plate 4.5.	SEM image of DH PG from Ardaman (2000). Field of view 15 microns.	95
Plate 4.6.	Backscatter electron images of HH PG showing quartz (dark grey), gypsum (mid- grey) and Cr-Fe grains (white – centre of picture) with energy dispersive spectra for the latter.	100
Plate 4.7.	SEM image of HH PG from Ardaman (2000). Field of view 15 microns.	101
Plate 4.8.	Backscatter electron image of quartz grain with inclusions of Ca, P and Fe phases.	103
Plate 4.9.	Backscatter electron image of quartz grain with inclusions of Fe,Mn phase.	103
Plate 4.10.	Backscatter electron image of quartz grain with inclusions of Ca, P phase and isolated barium sulphate crystal.	104
Plate 4.11	Element distribution map of sample GO-BS. Elements displayed separately. CP = backscatter image of sample.	104

Plate 4.12	30 tonne excavator sunk into perimeter dyke PG, Cell 1, Phosphate Hill, April 2000. The excavator body sank until it was floating on the base of the cabin and the bucket was also completely submerged in liquefied PG.	125
Plate 5.1	Phosphate Hill PG Stack – Constructing Cell 4 (Cell 2 behind), April 2003.	131
Plate 5.2	Flooding in Galah Pit, <i>circa</i> 1975. The water is estimated to be 8-10m deep along the right (eastern) side, becoming shallower to the left (west) and took several weeks to drain away.	168
Plate 5.3	Consolidation/shrinkage cracks developing in the top of Cells 1 and 2, Phosphate Hill, February 2004. The cracks are tens of metres long and 10-20cm wide. The height of the stack has dropped by about 1m in approximately six months.	178
Plate 5.4	Close-up of consolidation cracks in the centre of Plate 5.2. The surface crust that develops on the stack is clearly visible above the darker line and is 3-5cm thick.	179
Plate 6.1	Aerial Photo of Phosphate Hill PG Stacking Facilities Cells 1 (south) to 4 (north), with Galah North pit and fertilizer plant, 1 July 2003.	197

Abbreviations

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