

CHAPTER ONE

INTRODUCTION



Plate 1.2. Phosphate Hill PG Stack (Cells 1 & 2)

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1.0 INTRODUCTION

The global fertilizer industry is an integral part of an agriculture sector which is under pressure to continue to feed the steadily increasing human population. As demand for fertilizer increases so too does the production of a common by-product in the fertilizer manufacturing process: phosphogypsum (PG). Over one hundred millions of tonnes of this material is sent to storage facilities every year (Wissa 2001) with little prospect of being utilised on anything other than the very small scale (Anon 2002, Conklin 1992).

Despite on-going research into alternative uses for this material the sheer volume produced, combined with the radioactive impurities contained within much of the product, makes storage in gypsum stacks or disposal at sea the only viable options for dealing with this product (Heering and Zeldenrust 2000, USEPA1999, Johnson and Traub 1996). Few production sites utilise the ocean disposal method due to a combination of environmental factors and, generally, the processing facilities' distance from any suitable water body (Wissa 2001). Stacking on land is the more common solution to the storage/disposal problem, supported by the United States Environmental Protection Authority (USEPA 1999), and comes in two forms: dry stacking and wet stacking.

Dry stacking is where the hemihydrate (HH) (bassanite - $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) or dihydrate (DH) ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) form of PG is transported and stacked semi-dry, as it comes out of the production process, without the addition of any further fluids. It is currently used in the Middle East, Africa and some former Eastern Bloc states in Europe but has limitations to stockpile size and stability (Wissa 2001, Algroup Alusuisse 2001, Wissa *pers comm.* 2000). Wet stacking involves the mixing of the process product with fluid, with the resultant slurry being transferred into large (many hectares) storage basins where the solids settle out and the excess fluid is drained and usually re-used within the system. This pond-and-pile construction method is the more common method of PG storage, allowing for larger, more easily constructed stacks, and is used around the world (Wissa *pers comm* 2000, Anon 1998).

A fourth option for storage has been trialled in the United States and elsewhere: using PG as mine backfill. In this case, the PG is blended with clay tailings taken from the phosphorite beneficiation process and then pumped into the void. The mix, in which the PG is largely neutralised by the high levels of Ca in these particular clays, is allowed to dewater and consolidate before revegetation (Wissa 2001, Conklin 1992). At Phosphate Hill it has been suggested that the PG alone may be suitable as backfill for the mine. This study has been instigated to assess the viability of that possibility.

1.1 Purpose

In 1999 WMC Fertilizers (WMCF), a subsidiary of WMC Resources, opened a new fertilizer production plant at Phosphate Hill. Mining approximately 2 million tonnes of phosphorite ore per year, the facility produces about one million tonnes of fertilizer and ~1.4 million tonnes of PG per year. The short to medium term storage for this product is in wet stacks located to the north of the plant. However, difficulty in gaining access to more land for stacks has resulted in the Company considering other options. One of the long-term storage alternatives is in-pit disposal, filling the voids left after mining back to the local land surface, and it is for this purpose that this study has been undertaken.

In order for the PG to be effectively used as a mine backfill material, whether alone or as part of a mixture, its properties need to be known, with a particular focus on mineralogical, geochemical and dissolution characteristics. This knowledge allows those planning to use the material to judge whether it is physically and chemically appropriate for the proposed purpose and to identify what the short and long term effects of such use might be. As any storage facility will be a permanent addition to the landscape, the information required will include the long-term stability of backfilled areas when exposed to normal physical inputs such as rain and wind and the chemistry of any by-products that may result over any time span.

1.1.1 PREVIOUS WORK

The PG produced at Phosphate Hill was known from the start of operations to be

different from that produced at sites elsewhere in the world, in that it contained a higher amount of quartz, but no other information was available. Some basic analyses were carried out by Ardaman and Co. shortly after mining and fertilizer production began in late 1999 (Ardaman 2000) but these used a very small sample base and focussed particularly on the mechanical aspects of the material, to assess construction requirements for the stacks and their long-term viability. This thesis was instigated by the Company to define the PG mineralogically, chemically and morphologically, thus providing a base line for further study into the product and its possible uses.

Early in the production process at Phosphate Hill a number of projects were begun to look at the possibilities for reuse of the PG, rather than storage. These included selling the PG for use as part of a paste mixture for underground mine backfill, utilising it in agriculture or as a construction material. All of these studies were brief and on a small scale, and conducted without full knowledge of the character of the local PG. Although there was potential identified, the studies generally concluded that little more would happen with the material due to its impurities (including relict acids, heavy metals and radionuclides) and the prohibitive costs involved in shipping the PG, or any secondary product, the considerable distance from Phosphate Hill to such small markets. The results of this study may allow a reassessment of the feasibility of possible reuse of PG, whether in the short or long term.

1.1.2 PG PRODUCTION

PG production as a by-product of fertilizer manufacture has been a fact since the development of a large scale wet-process phosphoric acid industry after World War II (Becker 1989). The wet-processing of phosphate ores uses the process of acidulation, during which sulphuric acid attacks the ore to produce PG (plus impurities) and phosphoric acid, which are separated *via* filtration (EFMA 2000). There are two general methods of phosphoric acid production: one has a reaction temperature of 70-80°C and results in 26-32% P₂O₅ in the phosphoric acid and dihydrate PG (CaSO₄.2H₂O) while the other reacts at 90-110°C to give 40-52% P₂O₅ in the acid and hemihydrate PG (CaSO₄.½H₂O) (EFMA 2000). The plant at Phosphate Hill utilises a hemihydrate process at 98-100°C. The PG is then filtered from the acid and mixed

with acidic process water to convert the hemihydrate PG into dihydrate PG, which is then stored in above-ground stacks using the wet-stacking method.

The methods and technologies utilised in wet-process phosphoric acid production have constantly evolved in an effort to overcome inherent problems associated with crystal sizing, morphology and filtration, scaling, sludges and corrosion (Becker 1989). Crystal size and shape and good filtration are interlinked. As HH crystals in filter cake are very small and generally not well-formed, filtration of solids from acid can be difficult (EFMA 2000). The highest filtration efficiencies occur when the crystal size is kept consistent with shapes of a moderate surface-to-volume ratio and preferably including clusters to enhance acid drainage (Becker 1999). Scaling and sludges are the result of ongoing chemical reactions within the acidulation and post-acidulation phases (EFMA 2000). Corrosion of equipment, particularly in the HH system, occurs due to the higher temperatures used and stronger acid produced (EFMA 2000).

1.1.3 PG RESEARCH

PG itself has long been the subject of investigation. While these studies can include information on chemistry and mineralogy, with particular emphasis on the impurities contained within the material (rather than the pure gypsum phases) they generally focus on disposal methods and alternate uses for the product. The latter include reprocessing, agriculture, earthworks and construction. Another specialist area of research is on the radionuclides that the PG inherits from its parent phosphate ore and their potential effects on the environment.

Efforts at reprocessing PG generally focus on extracting purified sulphur and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). It is a high temperature process that, although successful, is rarely used as it is uneconomical when compared to the mined material (Korcak 1998, Johnson and Traub 1996, Conklin 1992). Although it has also been proven possible to remove and concentrate Ra-226 from PG using acid attack or calcining and filtering, again it is uneconomical, with little interest from the market, and creates problems with the storage of the product (Conklin 1992, Moisset 1990, 1986).

Agriculture provides many more options for recycling PG and thus has been subject to greater levels of research. The material works on several levels in the soil, including inhibiting crusting and minimising erosion at the surface through ameliorating subsoil acidity to directly benefiting plant growth, yield and quality. Erosion control and crusting inhibition using PG is achieved due to its high dissolution rate adding electrolytes to the soil which promote flocculation and inhibit clay dispersion, thus enhancing soil permeability and infiltration rates and maintaining a rough soil surface (Chan *et al.* 1999, Ramirez *et al.* 1999, Al-Oudat *et al.* 1998, Agassi and Ben-Hur 1991). This is a particularly effective treatment in soils containing smectite $((0.5\text{Ca},\text{Na})_{0.7}(\text{Al},\text{Mg},\text{Fe})_{4-6}[(\text{Si},\text{Al})_8\text{O}_{20}](\text{OH})_4.n\text{H}_2\text{O})$ and/or kaolinite $(\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8)$ but less so in mica (chemistry unspecified) and illite $(\text{K}_{1.5-1.0}\text{Al}_4[\text{Si}_{6.5-7.0}\text{Al}_{1.5-1.0}\text{O}_{20}](\text{OH})_4)$ bearing soils ((Buhmann *et al.* 1996, Stern *et al.* 1991a). Despite concerns to the contrary there is no evidence from the many studies of the agricultural use of PG that application of the by-product increases soil pH, acidification or liming and no significant results have been reported regarding radionuclide contamination (University of Florida 1996b, Conklin 1992).

PG is effective at treating subsoil acidity due to its rapid movement through the soil profile. Ca deficiencies are countered by an increase in exchangeable Ca and Al toxicity is reduced by precipitation of aluminium sulphate due to the increase in SO_4^{2-} (Toma *et al.* 1999, Wang *et al.* 1999a and 1999b, Alva and Sumner 1990). Soil and crop improvement can continue for up to three years after an application of PG due to movement of enriched leachate down through the soil profile (Alva *et al.* 1991, Alva and Sumner 1990).

The increase in porosity and improved chemical nature of PG treated soil has been shown to have a beneficial effect on root proliferation, density and depth of penetration and, thus, on yield and quality for a number of crops, ranging from onions to cotton, peaches and tobacco (Wang *et al.* 1999a and 1999b, Stanley 1992, Conklin 1992). Pasture quality and yield is also improved by the application of PG due to the high solubility of PG-sourced Ca and SO_4^{2-} , again with negligible increases in radionuclides in soil, water or crop (Rehcgigl *et al.* 1998b, University of Florida 1996a, Mullins and Mitchell 1990).

Another area of research that has shown promise is using PG in the earthworks and construction industries. When utilised as part of an aggregate with soil, cement, gravel, sand or fly-ash and followed by compaction, PG has been proven to perform as well as, if not better than, traditional materials utilised as road base (Korcak 1998, FIPR 1997, Conklin 1992). This is particularly so when it is used in wet weather or wet areas as the PG does not need to be dried out, as do traditional clay road bases (FIPR 1996b, Conklin 1992); however, PG alone as a road base in wet conditions is not recommended due to its tendency to disintegrate (Chang and Mantell 1990). A number of trial roads have been built in Florida, USA, which have been monitored for a number of years and none show any radionuclide trends that are outside the normal background fluctuations (FIPR 1997, Nifong and Harris 1993, Bandyopadhyay *et al.* 1990).

Cement binding for construction purposes has also been investigated with favourable results. Studies have shown that PG acts as an excellent fill in concrete aggregates, providing a stronger end-product with greater retardation and workability for areas such as roller-compacted concrete, pre-cast building elements and roads (Chang 1990, Khalis *et al.* 1990, Chang 1988). PG addition has also been beneficial in reducing or preventing corrosion in steel reinforcing material in cement and has no effect on product durability in wet situations or tensile strength (Chang and Mantell 1990, Lin *et al.* 1990). In fact, the addition of PG to cement mixes can be beneficial as it increases long-term hydration, speeds up setting times, counteracts shrinkages and increases strength, with no adverse affects over the long term (Roy *et al.* 1996, Ghafoori and Chang 1993, Beretka *et al.* 1990).

There are a number of other construction uses for PG. These include using it as part of a mix with cement and fly-ash to build artificial reefs or oyster clutch substrates (Wilson *et al.* 1998, Kalajian and Boueri 1986); mixing with limestone sand and Portland cement to manufacture high-strength masonry bricks with good compressive and flexural strength (Ahmadi and Chang 1990a, Nanni *et al.* 1986); and in the manufacture of plaster and plasterboard (Roskill 1997, Conklin 1992).

A large amount of recent research has been funded by the Florida Institute of Phosphate Research (FIPR). Since its inception as an independent state research

agency in 1978, the FIPR has provided support for researchers in five areas: phosphate mining, beneficiation, chemical processing and phosphogypsum, reclamation and public health (FIPR 2003). Currently more than 180 reports are available on the results of FIPR sponsored research, as well as access to a much larger library of publications on the same subjects (FIPR 2003). The majority of other research is university-based, with a small amount coming from within the industry.

1.1.4 LIMITATIONS ON PG RE-USE

Despite consistent results showing that the radionuclide and heavy metal content of PG rarely results in any elevation of levels in local air, groundwater or soil, concerns about contamination from radionuclides, fluorine compounds and heavy metals have resulted in the United States Environmental Protection Agency (USEPA) severely restricting the availability of the material for either further research or general use (Dooris and Martin 2000, USEPA 1999, Korcak 1998). The other major problem facing re-use of PG is one of volume. It has been stated that the total market for products derived from PG is around 2% of total production so any reuse, even at the highest rates, will barely make a dent in the global stockpile of this material (Conklin 1992, van der Heijde *et al.* 1990).

Almost all of the available research has concentrated on material derived from ore deposits and processing plants that are based in the northern hemisphere, particularly the industries in Florida, Morocco and the Middle East. There is very little literature on PG produced in Australia and none has been published on the by-product created at the WMCF operation at Phosphate Hill. This study will be the first full examination (mineralogy, chemistry, morphology) of the Phosphate Hill PG.

1.2 Location

Phosphate Hill is located approximately 130km SSE of Mt Isa, north-western Queensland, Australia (Figure 1.1). It is a remote area of black soil plains with mesas, buttes and bluffs the only prominent land features (Plate 1.3). The climate is cyclical, with “wet” and “dry” seasons. The majority of the regional annual rainfall of 294mm occurs during the hot summer period while the winters are largely dry and warm (Figure 1.2).

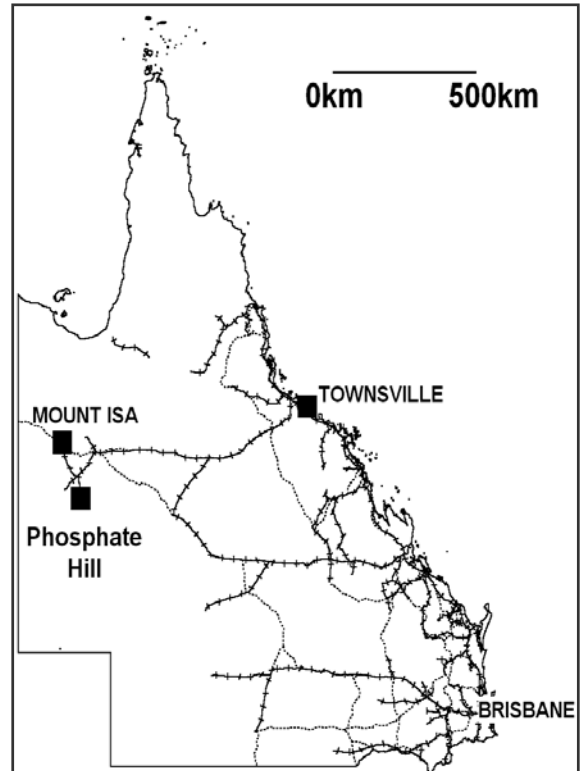


Figure 1.1. Location of Phosphate Hill (from Passmore and Berry 2002)

Vegetation predominantly consists of grasses and spinifex, acacias, dry sclerophyll eucalypts and river gums in the creek beds. Fauna is diverse and includes kangaroos, wallabies, dingoes, reptiles and a wide variety of bird life, as well as Brahmin cattle from the local stations and feral pigs, dogs, cats and camels. Flora and fauna, in addition to the human population on site and air, ground and water quality, are regularly monitored by WMCF staff to ensure compliance with company and government environmental guidelines, particularly in regard to the effect of fluorine ingestion.



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 landforms on the horizon.

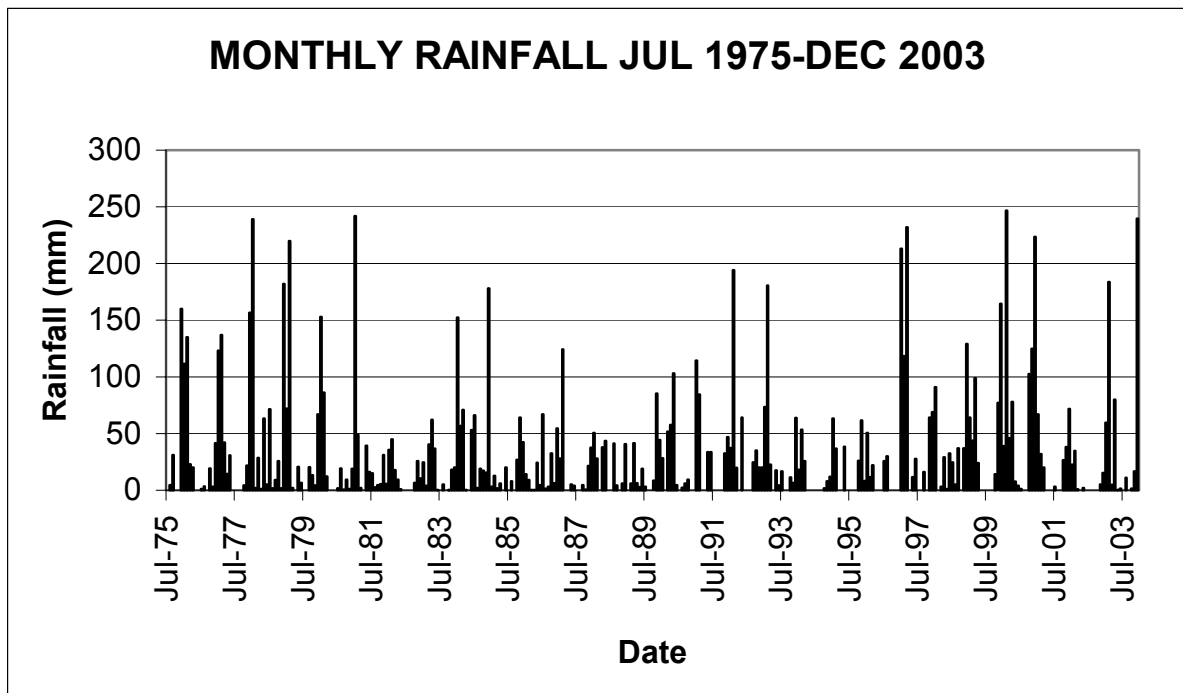


Figure 1.2. Graph of monthly rainfall in the Phosphate Hill area, 1975-2003. The cyclical nature of the seasons (wet and dry) is evident.

The monitoring program is particularly important around the phosphoric acid plant (PAP) and the PG stacks. The PAP is a source of gaseous fluorine compounds while the stacks, a potential source of dust, also exhale hydrogen fluoride gas and has the potential to pollute the local aquifer should its contained fluids or leachate escape from the stacking area. The aquifer is reasonably shallow (30-35m below surface at the time of writing), is of high quality and contained within very permeable and transmissive lithologies. It is the source of all water used at the WMCF operation, including the mining camp, and also provides water for the local cattle stations.

With up to 60 million tonnes of PG projected to be stored around the site by the predicted end of the operation (~30 years), with little likelihood of reuse or removal, the long-term possibility of pollution from the product is high. Above-ground stacks, such as those currently being constructed, can have some potential environmental impacts mitigated by using engineering solutions (*e.g.* capping the stack to prevent dust impacts on surrounding areas and the development of erosion channels). Many of the same impacts can be completely avoided by storing the PG below or level with the ground surface in areas such as the mine voids. However, the threat to the aquifer is much the same from either storage option should the relict acids and sulphate-rich leachate escape the storage facility into the groundwater with no neutralising agent present. The second part of this study will look at the leachate derived from different forms of PG found on site and examine the consequences of possible interaction between the leachate and the groundwater.