CHAPTER TWO

BACKGROUND

Plate 2.1. Phosphate Hill PG Stack (Cells 1 and 2) and Re-slurry Tank
March 2001
2.0 BACKGROUND

2.1 Introduction

This chapter will provide an overview of the site and plant operations at Phosphate Hill. Areas to be covered include geology, on a regional and local scale, the mining and stockpiling methods used to extract and store the ore and a brief outline of the processing plants involved in the production of the fertilizer product. Also included is an examination of PG stack construction methods as utilised at Phosphate Hill. This information is important for understanding the origin of the PG and under what circumstances the by-product is created, transported and stored on site.

2.2 PG Stacking

The WMCF fertilizer production facility, comprising beneficiation, phosphoric acid, ammonia and granulation plants, was constructed at its phosphate mine site at Phosphate Hill in 1998-1999. Mining commenced in May 1999 and the plant was commissioned in late 1999. The site achieved near-full production rates in mid-2000 and has been functioning at nameplate capacity since mid-2003. Wet-processing is used to manufacture both di-ammonium phosphate (DAP) and mono-ammonium phosphate (MAP) fertilizers from the local marine phosphorite ore and produces PG at a rate of about 0.71 tonnes per tonne of ore consumed. Current mining operations extract approximately 2 million tonnes of ore per year, therefore about 1.42 million tonnes of PG is sent to the stack in the same period (Wicks pers comm. 2003).

The first stack (Cells 1 and 2) was completed after three years of operation and contains just under five million tonnes of PG. Cell 3 is of small volume and is currently used only for excess acid water storage and recycling. Construction was completed on a second stack (Cell 4) with a ~5-year life in early 2003. PG deposition commenced later in that year and currently contains over 1 million tonnes of PG. During the projected life of Cell 4 studies will be finalised into the possibility of backfilling the mine voids with the PG by-product as part of the long-term Gypsum Close-Out Plan. The studies include a field trial, this research, other internal and external projects examining the
feasibility of various alternative uses for the by-product, and methods of safely decommissioning the current stacks for the long-term.

The current mining area is very close to the plant (within 500m at points), is up to 40m deep and is constantly expanding so it is an attractive target for PG stockpiling. The major problem faced by this proposal is that the ore body and its underlying lithological unit, part of a Cambrian marine basin sequence, also forms the local aquifer from which all water for the plant, camp and (to an extent) overlapping pastoral leases is drawn. As such, there is a reasonable probability of contaminants entering the local groundwater from any PG backfill.

As very little was known about the composition of the PG, this study was instigated in 2000 to mineralogically and chemically define it. The study covered PG slurry as it is currently deposited into the stack (dihydrate PG – CaSO$_4$.2H$_2$O - and acid process water), hemihydrate (CaSO$_4$.0.5H$_2$O) (HH) filtercake, aged dihydrate (DH) PG and the leachate recovered from the experiments carried out on the last two products.

2.3 Geology

This section will examine the geological setting and mineralogy of the ore body at Phosphate Hill.

2.3.1 REGIONAL SETTING

Phosphate Hill is located within the Lower-Middle Cambrian deposits of the Duchess Embayment. The latter is part of the Burke River Outlier which is appended to the Georgina Basin (Russell and Trueman 1971) (Figures 2.1 and 2.2). The work of Smith (1967) summarised the geology of the Georgina Basin and the following outline is drawn from that work and from Southgate (1983).

The Georgina Basin is a large (~324,000km$^2$) sedimentary basin that contains both marine sediments (dominantly carbonates) from the Cambrian and Ordovician and fresh water deposits (dominated by sandstones and siltstones) developed during the Devonian or Siluro-Devonian. Although a number of deformation episodes are evident in places,
with structures being locally intense in some areas, there is no evidence of metamorphism in any of the sequences. Precambrian sequences define all except the north-western and south-eastern margins. In the northern areas Cambrian strata from the Wiso and Daly River basins merge with the Georgina Basin sediments whilst in the south Cretaceous sediments of the Great Artesian Basin overlap those of the Georgina Basin. The phosphatic deposits of this Basin occur along the eastern side of the basin (in Queensland, including the Duchess Embayment – Figure 2.2) and in association with the Wonarah High (Northern Territory) (Green 1979, Cook and Shergold 1978).

**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.**
Figure 2.2. Regional geological setting for the eastern phosphogenic deposits of the Georgina Basin (after Rogers and Keevers, 1976)
The Burke River Outlier, of which the Duchess Embayment is part, is an appendage to the south-eastern side of the Georgina Basin (Figure 2.3). The Outlier itself is just under 100km long, ~30km wide and has been described by Russell and Trueman (1971) as a “graben containing mainly lower Palaeozoic sediments up to 5,000 feet [1500m] thick”. It is a shallow depositional basin that is fault bounded on all except its southern side where the sediments connect via a large trough to those of the Georgina Basin (Southgate 1983, Russell and Trueman 1971) (Figure 2.3).

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.
The exact physical relationship between the mostly marine Palaeozoic sediments within the southern and western zones of the Burke River Outlier and the marine and fresh water sediments within the Georgina Basin is obscured by the presence of the overlying Cretaceous continental successions of the Great Artesian Basin (Southgate 1983, Russell and Trueman 1971). Within the Outlier, the sedimentary sequences are the result of a series of marine transgressions and regressions that created shallow, narrow epeiric seas during which the phosphorite horizons were deposited (Southgate 1983, Cook and McElhinney 1978, Russell and Trueman 1971).

2.3.2 DUCHESS EMBAYMENT

The Duchess Embayment was a small, shallow, triangular shelf basin located on the faulted western side of the Burke River Outlier, separated from the main, deep-water basin of the Outlier by a major basement high (Thomson and Russell 1971, Russell and Trueman 1971). It is bounded on all three sides by faults (Western Fault, Rogers’ Ridge Fault and Mehaffy Creek Fault) and contains a number of other faults within it (Russell and Trueman 1971) (Figure 2.4). The Mehaffy Creek Fault is the eastern limit of the deposit and is believed to follow the hinge line on the basement high between the Burke River Outlier basin and that of the Duchess Embayment (Rogers and Crase 1979).

Regional folding has occurred to provide broad anticlines and synclines with dominantly north to north-west trends (Russell and Trueman 1971) (Figure 2.5). Some areas have undergone a secondary deformation event around east-west axes, resulting in local dome-and-basin morphology such as that seen at Phosphate Hill (Rogers and Crase 1979). On a regional scale, the Embayment dips approximately 5° to the east, although local structures can be much steeper (Rogers and Crase 1979) with complex interactions on the mine-scale.
Figure 2.4. Geology of the Duchess Embayment (from Rogers and Crase 1979).
The Embayment consists of a full cross-section of four of the six eastern Georgina Basin Cambrian lithosomes (Rogers and Crase 1979), a summary of which is presented in Table 2.1 below. These lithosomes occur in two forms: unweathered calcareous and weathered siliceous, with the ore body being 8-12m thick. The sequences mined at Phosphate Hill are the Cainozoic alluvium cover (unconsolidated sediments) and siliceous Inca Shale (overburden) together, and the siliceous Monastery Creek Phosphorite Member (MCPM - ore) (Wegner 2000) (Figure 2.6). Any PG dumped
directly in-pit would thus be exposed to the overburden and the ore body on the sides of
the pit void and the Lower Siltstone Member at the base of the void.

<table>
<thead>
<tr>
<th>AGE FORMATION UNIT DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cainozoic Sediments</td>
</tr>
<tr>
<td>Red-brown, clay-rich alluvium; chert rubble of variable thickness. Overlain by sandy soil. Some calcrete and phoscrete. <strong>UNCONFORMABLY OVERLIES:</strong></td>
</tr>
<tr>
<td>Lower Ordovician Swift Beds (SWF)</td>
</tr>
<tr>
<td>Ninmaroo Formation (NLST)</td>
</tr>
<tr>
<td>Middle Cambrian Inca Limestone (ILST)</td>
</tr>
<tr>
<td>Inca Shale (IS)</td>
</tr>
<tr>
<td>Lower-Middle Cambrian Beetle Creek Formation (BCF)</td>
</tr>
<tr>
<td>Phosphorite, phosphatic cherty siltstone, chert, fetid phosphatic limestone. Fresh calcareous and weathered silicic facies. M ax. thickness 37m. <strong>GRADATIONAL contact with LSM.</strong></td>
</tr>
<tr>
<td>Lower Siltstone Member (SM)</td>
</tr>
<tr>
<td>Lower-Middle Cambrian Thorntonia Limestone (TLST)</td>
</tr>
<tr>
<td>Silicified carbonate rock and coquina. M ax. thickness 12m.</td>
</tr>
<tr>
<td>Carbonate Member</td>
</tr>
<tr>
<td>?Upper Proterozoic-Lower Cambrian Mount Birnie Beds (MBB)</td>
</tr>
<tr>
<td>Ferruginous silty mudstone. M ax. thickness 18m.</td>
</tr>
<tr>
<td>Orthoquartzite Member (OQTZ)</td>
</tr>
<tr>
<td>Sandstone Member (SST)</td>
</tr>
<tr>
<td>Dolomite Member (DOL)</td>
</tr>
<tr>
<td>Tilloid Member</td>
</tr>
<tr>
<td>Lower Proterozoic Kalkadoon Granite (KG)</td>
</tr>
</tbody>
</table>

Table 2.1. Duchess Embayment stratigraphy at Phosphate Hill (after Russell and Trueman 1971)
2.3.3 ORE BODY – MONASTERY CREEK PHOSPHORITE MEMBER

The ore at Phosphate Hill is drawn from the full section of the Monastery Creek Phosphorite Member (MCPM), the upper unit in the Beetle Creek Formation (BCF). The phosphorite beds consist of weathered, siliceous, peloidal and collophane carbonate-fluorapatite with gangue minerals including iron hydroxides, clays and silica, which can occur in either indurated or friable beds (Plate 2.2) (Hough, 2002, Russell and Trueman 1971). The peloidal form consists of dominantly ovulitic cryptocrystalline carbonate-fluorapatite pellets that are irregularly shaped, spherical to sub-spherical and often contain contaminants such as iron hydroxides and organic material (Plate 2.3) (Hough 2002, Wegner 2000, Russell and Trueman 1971). Phosphatised bioclasts (shells, trilobites) also occur and the whole is variably cemented with microcrystalline chert in indurated beds or remains as friable phosphate “sand” in poorly consolidated beds (Hough 2002, Wegner 2000). Geochemical studies of rare-earth elements in the ore suggest that phosphatisation would appear to have occurred...
close to the seawater-sediment boundary with initial precipitation of francolite \( \text{Ca}_{10-a-b} \text{Na}_a \text{Mg}_b (\text{PO}_4)_{6-x} (\text{CO}_3)_{3y-z} (\text{CO}_3 \text{F})_x (\text{SO}_4)_z \text{F}_2 \) (Hough 2003).

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.
The other form in which the apatite occurs is beds of collophane mudstone that are infrequently distributed throughout the ore body (Wegner 2000, Russell and Trueman 1971). This occurs as beds of cryptocrystalline (<1 micron) carbonate-fluorapatite which can display radial patterns that may be microbial in origin (Plate 2.4) (Hough 2002, Wegner 2000). Often, the upper surfaces of these beds are covered by a thin veneer of glauconite \( ((K, Ca, Na)_{0.6} (Fe^{3+}, Al, Mg_{4.0} Fe^{2+})_{4.0} Si_{7.3} Al_{1.7} O_{20}(OH)_{4}) \) (Plate 2.8) (Hough 2003, Wegner 2000). Interbedded with the phosphatic horizons are mildly phosphatised cherts, siltstones and shales (Plate 2.2) which, together with iron hydroxide alteration minerals and areas of deeply weathered clays, form contaminants in the fertilizer production process.
Recent studies by Hough (2003, 2002), Mascini (2001) and Wegner (2000) have confirmed that the MCPM is the result of reworking of the primary peloidal deposits by wave and water action under highly variable conditions. This was followed by primary
carbonate cementing during early diagenesis, silicification during late diagenesis and a final stage of weathering which has removed organics and the primary carbonate matrix (Table 2.2).

Table 2.2. Diagenetic and weathering paragenesis for the MCPM (from Hough 2003).

<table>
<thead>
<tr>
<th>Sedimentation</th>
<th>Diagenesis</th>
<th>Weathering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithologies</td>
<td>Depositional Energy</td>
<td>Early compactional diagenesis</td>
</tr>
<tr>
<td>Grainstone</td>
<td>High-energy discrete</td>
<td>Micritic packstone</td>
</tr>
<tr>
<td>Phosphorite</td>
<td>Low-energy mixed carbonate</td>
<td>Peloidal micritic limestone</td>
</tr>
<tr>
<td>Mudstone</td>
<td>Low-energy mixed carbonate</td>
<td>Dental algal micrite</td>
</tr>
</tbody>
</table>

The phosphorite beds are variably associated with cherts, siltstones and shales which reflect changes to the depositional environment (Russell and Trueman 1971). These occur as thin (mm scale) beds within the phosphorite horizons but can also occur as substantial entities in their own right, such as the Unit 3 marker chert, a triple layer of phosphatised chert up to 30cm thick that defines the base of Unit 3 throughout the ore body (Plate 2.2, Figures 2.6 and 2.7) or Units 7 and 9 which are groups of thin beds of siltstone that can have a combined thickness of >30cm, with minimal phosphate content. As a result, individual units have differing grades of phosphate and volumes of gangue minerals (expressed as %P₂O₅, %Fe₂O₃ and %Al₂O₃), with the odd-numbered ones generally being significantly lower grade due to higher levels of chert, siltstone and shale. Those with even numbers consist of relatively pure phosphorite and thus have much higher grades (Figure 2.7). Phosphate-poor beds cannot be removed during mining and thus form contaminants which instead need to be removed during the production process.
Figure 2.7. Stratigraphic column of the Monastery Creek Phosphorite Member displayed in Figure 2.6 showing typical grades for $P_2O_5$, $Fe_2O_3$ and $Al_2O_3$ per Unit.
2.4 Hydrogeology

The Duchess Embayment has been the focus of hydrogeological study since the 1970s. Early drilling suggested that the aquifer was associated with the BCF and that the highest quality, most freely-available water was contained within the siliceous (weathered) facies. Broad delineation of the aquifer has been done to confirm this using a mixture of drilling (1960s to the present) and geophysics (down-hole wireline logging in the 1970s, 1990s and 2000, transient-domain electromagnetics (TEM) in 1990 and 2002 and nuclear magnetic resonance (NMR) in 2002) and the resulting outline of the siliceous facies within the Duchess Embayment is illustrated in Figure 2.8 below.

The earliest report extant to provide any specific results (Stewart and Passmore 1977) was on Stage 2 of the groundwater development program for the initial mining of the site by BH South. It reported the results of pumping tests carried out on a number of production bores located in what is still the primary borefield for the operation. This borefield follows an approximate 340° trend along the line of the Russell Fault (Figure 2.9). The 1977 pumping tests saw bores tested using either a Step Rate Test to evaluate hydraulic properties by pumping at three to five different rates for one hour each or a Constant Rate Test where pumping was for between 48 and 183 hours. Water levels were measured in specially constructed monitoring bores elsewhere within the aquifer to assess draw-down induced by the pumping. Analysis of the results using Jacob’s straight line method gave transmissivity rates of between 380-4959m²/day and the plotted draw-down results strongly suggested a laterally extensive, homogeneous aquifer contained within both members of the BCF.

More extensive reports on the Duchess Embayment Aquifer (DEA) are available from 1985 onwards. Rockwater 1985, 1990, 1996 and 2002 and PPK 2001a all report the results of further pumping tests from bores and sumps, observations of pit flooding events (Rockwater 1985) and water chemistry while PPK 2001b analysed core fracture patterns in diamond drill cores along with down-hole (neutron) geophysics results. Webb 1990 and Allen 2002 report on TEM groundwater investigations and Annison 2002 provides the results of the NMR aquifer survey.
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.
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 pers. comm.. 2004.
All of the reports have similar findings with regards to hydraulic conductivity being an average of 70m/day and a transmissivity average of 2000m²/day (derived from the rate of flow/discharge (m³/day) under unit hydraulic gradient (dimensionless) per unit area (per m²) multiplied by the aquifer thickness (m), or m³/day/m² x m (Moncrieff pers. comm. 2004)) has been drawn from the data contained in all the reports. The reports are also unanimous in saying that the siliceous facies is the primary host of the groundwater, which is contained within the many fine joints and bedding partings of the BCF as well as within the very porous friable phosphorite contained within the MCPM, with the permeability being slightly higher in the MCPM due to the presence of the friable material. The Inca Shale is identified as of low permeability and acting as an aquiclude above the aquifer, as does the Mount Birnie Beds below the BCF. Specific yield has been identified (Rockwater 1985, PPK 2001a) as being in the range 0.02 to 0.07. The boundaries of the aquifer are defined as the same as those of the Duchess Embayment, with crystalline Precambrian granites to the west and Ordovician limestones to the east, the latter separated from the Duchess Embayment by the impermeable Mehaffey Creek Fault.

Depth to the top of the water table was identified early (Rockwater 1977) as being about 30m below the surface and this has since been confirmed by drilling and by the 2002 NMR program (Annison 2002). The geophysics programs (Annison 2002 and Allen 2002) also confirmed Rockwater 1985 and PPK 2001a deductions that the average thickness of the aquifer is 30m but it can be up to 50m thick while it is truncated to the north (around an east-west line just north of 21°50’ on Figure 2.8) by a basement high intersecting the average (pre-mining) SWL of 234mRL. All reports agree that recharge is the result of infiltration of flood runoff at the intersection of Dead Horse and Galah Creeks (between Galah South and Brolga pits) and in other areas where the BCF crops out around the margins of the Duchess Embayment, with an annual estimated rate of between 400 and 800 megalitres/year (Rockwater 1985, PPK 2001a). With mining opening new voids into the BCF recharge rates are expected to increase.

Drawdown of the aquifer within the Embayment has been shown in all reports since Rockwater 1977 to be extremely flat due to the very high transmissivity of the BCF. Current quarterly bore monitoring rounds confirm this, meaning that selective dewatering for pit operations is not possible and dewatering needs to be planned to
target the aquifer as a whole. A natural flow direction of north to south has been identified in the aquifer (Rockwater 1985, 1990) and this is exacerbated by pumping (see Figure 5.12). There is believed to be minor eastward and westward flow occurring after flood events due to a low mound underlying the intersection of Dead Horse and Galah Creeks but most of the mound effect rapidly disappears after recharge (Rockwater 1985).

Water quality has been tested extensively since the 1970s and the results are contained within the groundwater monitoring database held by WMCF. The results have been very consistent over the years and a summary of them is presented in Table 5.8. The water tends to be mildly alkaline (average pH of 7.5) but otherwise is of very good quality, with low total dissolved solids and chlorides.

2.5 Production Process Overview

The fertilizer production technique at Phosphate Hill utilises the Hydro Hemihydrate wet-processing method (Gobbitt and van Ede, 2004). The steps involved in this are as follows.

2.5.1 MINING METHOD AND STOCKPILE MANAGEMENT

Ore is currently sourced from four pits: Galah (north end of ore body) Brolga (central), Corella (south central) and Jabiru (south), with a fifth (Magpie) due to come on line north-west of Corella in 2004. The mining method begins with all overburden being removed from the top of the ore seam in the chosen parcel area, following the natural contours of the structures (dome-and-basin morphology), and stored in waste stockpiles located close to and within the pits (Figures 2.8, 5.10). Strong clay alteration/weathering products (referred to as dissolution and containing little or no phosphate), which can clog screens in the beneficiation plant and affect the morphology and chemistry of the PG, reducing PAP recovery levels, are usually found at this stage and are removed by the excavator under the direction of geological personnel and sent to the waste stockpiles. Once the waste stockpiles have reached full capacity and are not longer in use they are rehabilitated, using engineering to minimise rain runoff and erosion and seeded with local plants to assist with the natural revegetation process.
The ore is mined in discrete parcels based on the 20m x 20m grade control drilling carried out every year. The total volume of each parcel can range from ~80,000 tonnes to ~140,000 tonnes, dependent upon the needs of the plant. A parcel is extracted in 3m thick, flat flitches (levels), consisting of 2-3 ore units, to begin the grade mixing process, with any further high dissolution and/or iron hydroxide zones being removed where necessary. At the bottom of the ore body mining again follows the contours of the structures that control the shape of the ore (Plate 2.6). This is done under the supervision of members of the Geology Department or fully-trained excavator operators in order to minimise dilution or loss of ore.

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.

The ore is held in stockpiles on the ROM (Run of Mine) pads (Figure 2.10) that are built via longitudinal lines in a number of lifts up to total heights of nine metres and contain up to 140,000 tonnes of rock (Plate 2.7). Recovery of the ore for feeding occurs
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.

Latitudinally across the stockpiles in order to further homogenise the grade of the ore and reduce grade spikes or troughs in the feed entering the fertilizer production process.
at the beneficiation plant. The ore is fed via a loader through the hopper into the primary crusher and the beneficiation circuit.

2.5.2. BENEFICIATION PLANT

The ore passes through three stages of crushing in the beneficiation plant before it is reduced to sub-25 micron size in the ball mill (Figure 2.11). The pulverized rock is washed during this stage to remove as many of the contaminants (iron hydroxides, clays, minor quartz) as possible. Some P₂O₅ is lost in this part of the process, with average phosphate recoveries in the beneficiation plant falling in the range of 87-93%. The by-product is pumped into holding (slimes) dams and the cleaned rock is sent via the thickener to the three storage tanks (Figure 2.11, Plate 2.8) where the final mixing and homogenisation of the grade takes place.

Figure 2.11. Phosphate Hill beneficiation plant process flow chart (from WMCF Intranet live production pages).
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.

The rock slurry is fed into the phosphoric acid plant from the storage tanks.

2.5.3 PHOSPHORIC ACID PRODUCTION

The phosphoric acid plant (PAP) at Phosphate Hill is the largest single-line hemihydrate plant in the world (Gobbitt and van Ede 2004). Its process flow chart is shown in Figure 2.12. The rock slurry enters the PAP circuit via a series of rock filtration belts which remove the majority of the water from the slurry. The rock filter cake is then dropped into the reactor chain where it undergoes acidulation in two stages, the first with recirculated phosphoric acid (H$_3$PO$_4$) and the second with 98.5% strength sulphuric acid (H$_2$SO$_4$) (see 2.3.5 below) at 98-100°C. This reaction produces phosphoric acid and hemihydrate phosphogypsum (PG) (CaSO$_4$·½H$_2$O) through the principal reaction:

\[ \text{(1)} \quad \text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2 + 10\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow 10\text{CaSO}_4·0.5\text{H}_2\text{O} + 6\text{H}_3\text{PO}_4 + 2\text{HF}. \]
The reaction occurs in two steps. This is done to minimise reaction blocking, an effect that occurs when phosphorite and H$_2$SO$_4$ are reacted directly with each other. Such a reaction will cause in insoluble layer of gypsum to form on the surface of the rock particles, self-limiting the acidulation process. As a result, the rock particles are first acidulated in reactors 1A, 1B and 1C with recirculated H$_3$PO$_4$ to convert as much rock as possible to monocalcium phosphate (Ca(H$_2$PO$_4$)$_2$) (reaction 2). The Ca(H$_2$PO$_4$)$_2$ is then further acidulated in Reactor 2 with H$_2$SO$_4$ to form more H$_3$PO$_4$ and precipitate gypsum (reaction 3) as hemihydrate. A simplified illustration of the process made without reference to the final hydration state of the PG (below) comes from Anon 1999.

(2) \[ \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 14\text{H}_3\text{PO}_4 \rightarrow 10\text{Ca(H}_2\text{PO}_4)_2 + 2\text{HF} \]

(3) \[ \text{CaH}_4(\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + \rightarrow \text{CaSO}_4 + 2\text{H}_3\text{PO}_4 \]

Following the acidulation process the phosphoric acid is separated from the PG waste product over four filter belts. The PG is transferred via overland conveyor belt to the re-slurry and storage facilities while the phosphoric acid is sent to storage tanks (Plate 12) for concentration and injection into the granulation plant for final fertilizer production.

Figure 2.12. Phosphate Hill phosphoric acid plant process flow chart (from WMCF Intranet live production pages).
Fluorine is liberated from the apatite during the acidulation process. This generally occurs as hydrofluoric acid (HF) which is removed from the reactors in cooling water or gases (EFMA 2000). The latter are then scrubbed to removed as much of the HF as possible. However, relict fluorine can also react with SiO₂ to form other compounds, such as hydrofluoric acid (HF), silica tetrafluoride (SiF₄) and fluorosilicic acid (H₂SiF₆). Both of these are found at Phosphate Hill. They are the result of a series of reactions, summarised below from EFMA 2000:

\[
(4) \quad \text{CaF}_2 + 2\text{H}^+ \rightarrow 2\text{HF} + \text{Ca}^{2+} \\
(5) \quad 4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \\
(6) \quad 3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SiF}_6 + \text{SiO}_2
\]

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.

Other side reactions occurring concurrently in the reactors involve calcium fluoride (CaF₂) and calcium carbonate (CaCO₃), with both reactions leading to increased
consumption of \( \text{H}_2\text{SO}_4 \) and increased production of \( \text{HH} \) (Anon 1999). These reactions are:

\[
\begin{align*}
(7) & \quad \text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4 \\
(8) & \quad \text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{CaSO}_4 + \text{H}_2\text{O}
\end{align*}
\]

The hydration state of the gypsum produced by these reactions is dependent on both the reaction temperature and the concentration of the phosphoric acid. This is shown in the phase diagram in Figure 2.13 below, taken from Gobbitt and van Ede 2004:

![Phase diagram controlling gypsum species formation in phosphoric acid plants](image)

**Figure 2.13** Phase diagram controlling gypsum species formation in phosphoric acid plants (from Gobbitt and van Ede 2004).

\( \text{P}_2\text{O}_5 \) recoveries in the PAP average around 90%, with the losses occurring in several ways. The three major loss classifications (from Becker 1989) are as acid losses to the PG filter cake and during mechanical effects such as plant washing; as co-crystallised \( \text{P}_2\text{O}_5 \) in the PG crystal pattern; and as unreacted rock particles due to the self-limiting nature of the acidulation process using \( \text{H}_2\text{SO}_4 \). With the exception of the recirculated plant wash water, all of these losses are delivered directly to the gypsum stack in the PG filter cake.
Fe$_2$O$_3$ tends to remain in the H$_3$PO$_4$ and thus in the fertilizer product at ~2% in DAP and ~3% in MAP (Table 2.3). Minor amounts of most other elemental species are also retained in the H$_3$PO$_4$ and thus in the fertilizer product (see 2.5.4 below).

2.5.4 AMMONIA AND GRANULATION PLANTS

The third plant located on site at Phosphate Hill is the ammonia production facility. Although not directly related to the processing of the ore or the handling of PG it is a vital component of the fertilizer manufacture process as it provides the ammonia required for the finished product, di-ammonium phosphate (DAP – (NH$_4$)$_2$HPO$_4$) or mono-ammonium phosphate (MAP – NH$_4$H$_2$PO$_4$).

![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.](image)

The ammonia plant process flow chart is shown in Figure 2.14 and consists of hot and cold processing streams. It takes natural gas, sourced from the gas fields of south-western Queensland, and, in the hot processing side, through a catalytic reaction with steam, generates hydrogen. On the cold process side, nitrogen that has been cryogenically separated from the atmosphere, is stored separately. The hydrogen and
nitrogen are compressed and reacted to create the ammonia, which is then removed by refrigeration with any un-reacted components being recirculated through the system. The ammonia is then stored in a refrigerated, double-skinned pressure tank (Plate 2.10) before use in the granulation plant.

![Image of Phosphate Hill ammonia plant]

**Plate 2.10. Phosphate Hill ammonia plant.**

The fourth plant on site is the granulation facility. The plant at Phosphate Hill is the largest single-train granulation plant of its kind in the world. Its process flow is illustrated in Figure 2.15. Here, the phosphoric acid and ammonia are injected into the granulator with feed stock (sand or undersize fertilizer grains) to form the fertilizer pellets. These are then dried, screened, cooled and coated with oil before being sent to storage for on-shipping *via* rail and sea to the local and international markets. Colouring can be added during the manufacturing process, if required.
Figure 2.15. Phosphate Hill granulation plant process flow chart (from WMCF Intranet live production pages).

Plate 2.11. Granulation plant and storage shed, Phosphate Hill.

The major form of fertilizer produced at Phosphate Hill is DAP (18% N, 46% P₂O₅) with lesser amounts of MAP (11% N, 52% P₂O₅). In-house analysis of the fertilizer product shows that other elements are also present, albeit at very low levels (Table 2).
Table 2.3. Average element analyses, Phosphate Hill DAP and MAP.

A comparison of the results in Table 2.3 against those for the PG presented in Tables 5.2 (major elements) and 5.4 (trace elements) reveals that, in addition to P₂O₅, many of the species are retained at higher levels in the fertilizer product than in the PG. These include Al₂O₃, Fe₂O₃ and MgO among the major elements and Ag, Cd, Co, Cr, Cu, Mo, Ni, Pb, Rb, U, V and Zn among the trace elements. K₂O, MnO, Na₂O and TiO₂ are found at similar levels in both fertilizer and PG.

2.5.5 SULPHURIC ACID PLANT

The sulphuric acid used in the acidulation process in the PAP is derived from three sources. These are acid purchased directly from the Sun Metals refinery in Townsville, pure sulphur sourced from Canada and acid produced in the WMCF Sulphuric Acid Plant in Mt Isa. The latter is the primary source. At this plant site, unused SO₂ gas from the Xstrata copper smelter that would otherwise be discharged to the atmosphere is captured by the WMCF operation (Plate 2.12) where it is cleaned by passing through a quench tower and radial flow scrubbing system. From there it is converted to H₂SO₄ through a system of cooling, precipitation and drying (see process flow chart, Figure 2.16) before shipment by train to site. Maximum acid production rates are 4,200 tonnes per day, giving a yearly capacity of over 1.5 million tonnes.
Figure 2.16. Mt Isa sulphuric acid plant process flow chart (from WMCF Intranet live production pages).

The plant can also burn pure sulphur to produce acid as a back-up supply when the Xstrata smelter is off-line. Up to 250,000t of acid is also purchased per year from Sun Metals, from whence it is shipped by train directly to Phosphate Hill. The rail system consists of GATX tank rolling stock which feature a single load/unload point to minimise potential safety hazards associated with loading and unloading acid. At Phosphate Hill the acid is unloaded and stored in three tanks for feeding directly into the PAP process.
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.

2.5.6 PG STACKING METHOD

PG storage at Phosphate Hill uses the wet stacking method. The process flow chart is illustrated in Figure 2.17. The first step of stack construction is that the hemihydrate PG enters the re-slurry tank where it is mixed with acidic waste process water from the plant and returned water drained from the stack. Plate 2.1 shows the overland PG conveyor, re-slurry tank and stack in 2001. Plate 2.13 shows the slurry being mixed in the re-slurry tank.
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.

This step starts the conversion of the hemihydrate PG \((\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O})\) to dihydrate PG \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\). The slurry is then piped to a discharge point (spigot) in the stack.
Figure 2.17. Phosphate Hill PG stack process flow chart (from WMCF Intranet live production pages).

The following summary of pond-and-pile wet PG stack construction as followed at Phosphate Hill is adapted from Ardaman 1999 and illustrated in Figure 2.18.

The initial slurry discharge is into a sedimentation pond contained within a perimeter earthen starter dyke lined with 3mm thick high-density polyethylene (HDPE), where the conversion of hemihydrate to dihydrate continues to completion. The discharge continues until sufficient PG has settled in the pond next to the starter dyke to allow some of it to be excavated and cast on top of the sedimented PG. It is then compacted and shaped to form a new, elevated starter dyke that is high enough to contain the deposition of additional slurry. The new slurry refills the previous excavation and is used to construct the next lift of the starter dyke. The slurry discharge spigot/s can be moved to ensure that the elevation of the stack is on an even level.
Figure 2.18. Schematic of PG wet-stack construction method as used at Phosphate Hill (adapted from Ardaman 1999).

A peripheral elevated rim ditch is used to distribute the slurry around the perimeter of the stack and is created by casting a small inner dyke inward from the starter dyke. A sluice is cut into the inner dyke to allow the slurry water and finer particles to flow into the centre of the sedimentation pond while the coarser sized particles are retained in the rim ditch within reach of the excavator (Plate 2.14). The rim ditch improves the uniformity of PG deposition within the stack and eliminates the need to drain the pond.
to facilitate construction as the material excavated for the perimeter dykes will generally be above the water level in the pond.

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.

The stack is built with underdrains constructed in the floor. Over time the acid water component of the PG slurry drains through the crystalline PG of the stack and is directed through the underdrains into the return surge ditch (Figure 2.17). Once there it is returned to the re-slurry tank for re-use.

This construction method continues until the stack reaches capacity, at which time a new stack (or cell) is started. At Phosphate Hill the original two stacks (Cells 1 and 2) were joined to form one stack in 2002 and have now been closed as they have reached full capacity. Cell 3 is a holding pond for excess process water and Cell 4 is the currently active stack.

Because the current methods build stacks that are prominently elevated above the surrounding terrain there are a number of short and long term environmental issues that
are associated with them. These include erosion and dusting, mass failures and other stability issues, and the potential for contamination of the surrounding areas both on the surface and into the groundwater should the liner fail. The current construction method includes manicuring of the outer walls of the stack during construction, to keep the walls as smooth as possible in order to minimise the opportunities for erosion to begin. This is the only stacking facility in the world where this takes place (Royal pers. comm. 2003). However, alternative disposal strategies are under investigation by WMCF and include capping the stacks, re-use of the material and disposing of the PG below the current ground level in the mining voids. It is for this latter option that this study has been undertaken.

The Cambrian marine phosphorite sediments mined at Phosphate Hill are the major source of components in the PG with the remainder derived from the acids used during the acidulation process. Through the system of crushing, washing, acidulation, ammonia injection and granulation ammonium phosphate fertilizers are produced for export around the world while the PG by-product is stored on site in facilities built according to well-established wet-stacking methods. This study will provide the physical and chemical characterisation of the PG needed to fully assess the applicability of alternative disposal methods to the Phosphate Hill site.