CHAPTER THREE

METHODOLOGY

Plate 3.1. Phosphate Hill PG Stack (Cells 1 and 2) and Re-slurry Tank
April 2002

3.0   METHODOLOGY

3.1   Introduction

When fertilizer and PG production commenced at Phosphate Hill in late 1999 it was quickly noted that the PG seemed to be different to that produced at similar plants elsewhere in the world. Initially, it was felt that the apparent difference may have an impact on stack construction methods, so a small test was done on the PG, focussing primarily on the mechanical properties of the material but also including a chemical analysis of the single round of PG samples taken. The results were summarised in Ardaman 2000 with the conclusion being that the greater amount of quartz (SiO_2) found within the Phosphate Hill PG should not be an issue to stack stability provided the quartz was not allowed to build up in discrete areas or layers within the stack. The current construction methods do not allow this to happen.

Early in the projected life of the operation alternatives to above-ground stacking were already being considered. One of the more favoured options was in-pit disposal, where PG would be dumped in the voids left after mining operations were completed in a given area. This idea was complicated by the interaction of the local aquifer with the ore body sequence over much of the resource. As such, it was felt that a full study should be instigated to fully characterise the physical and chemical properties of the varieties of PG available for use as fill, providing important base line information for future work on the product.

This study is the result of that decision. It will not only characterise the material but specifically look at the possible pollutants that are present and may be mobilised into liquids if the PG is deposited directly into the mine void in addition to the changes that may occur to the fill material as part of the leaching process. Exposure to the elements, specifically high rainfall wet seasons, and natural draining of relict liquid from within the PG are seen as the most likely source of escaping fluids.

A sampling program was instigated to analyse:

(a)   PG slurry over a 12 month cycle, to assess any differences in slurry product through a full cycle of seasons or resulting from different ore sources. An additional sample was taken late in the program for further radionuclide analysis; and

(b)   "dry" PG in its two forms of HH (directly off the filter belts from the phosphoric acid plant into the re-slurry tank) and DH (sampled from the stack itself after the draining of excess liquid had taken place). The latter was sampled as both newly deposited material and that which had been on the stack for at least six months.

In addition to this, three types of PG were subjected to dissolution in fresh water and both the analyte and the post-dissolution PG sampled. Methodologies for each experiment are listed below:

3.2   PG Slurry Sampling

Discussions were undertaken with the Superintendent – Gypsum and other PG stack staff as to the best location for sampling of slurry. It was decided that, initially, the point at the end of the launder (Plate 3.2), where the slurry actually enters the pond on the stack directly from the re-slurry tank (Plate 3.3), would give the best possible sample with the least bias.
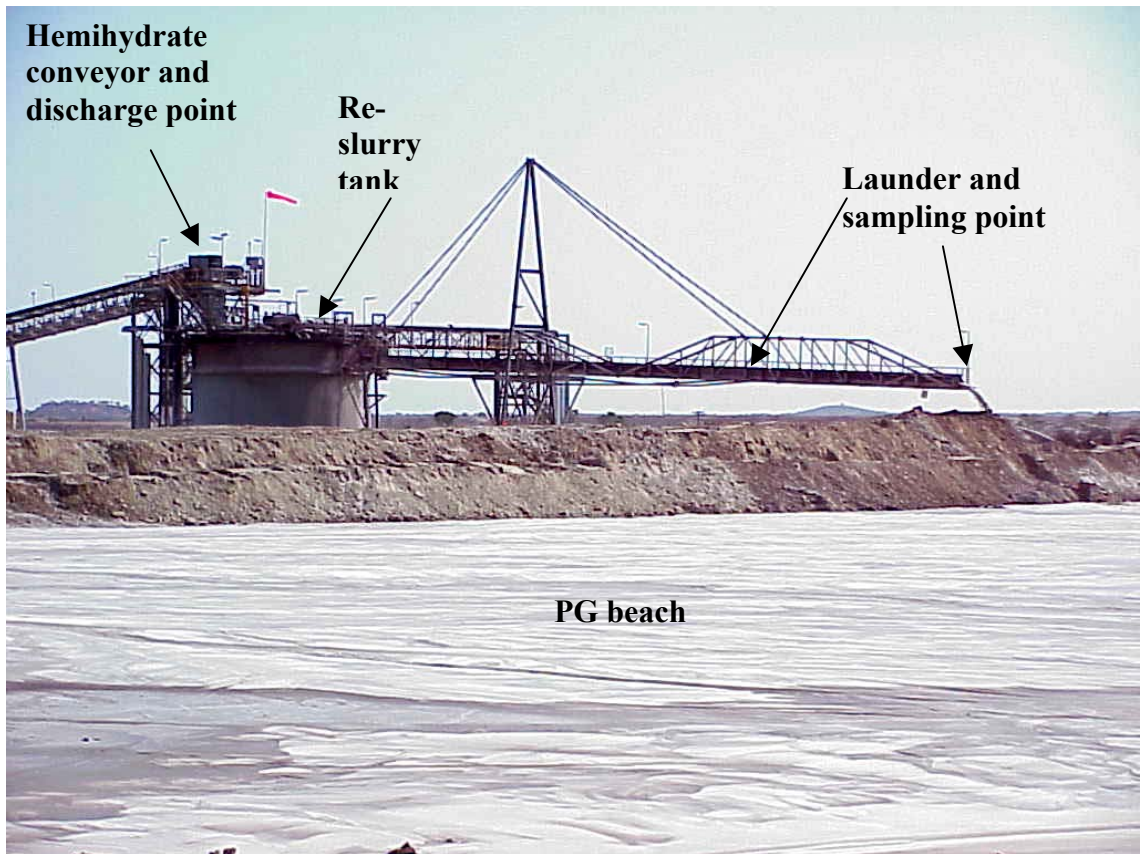
Plate 3.2. Re-slurry tank and launder discharging into Cell 1, October 2000.
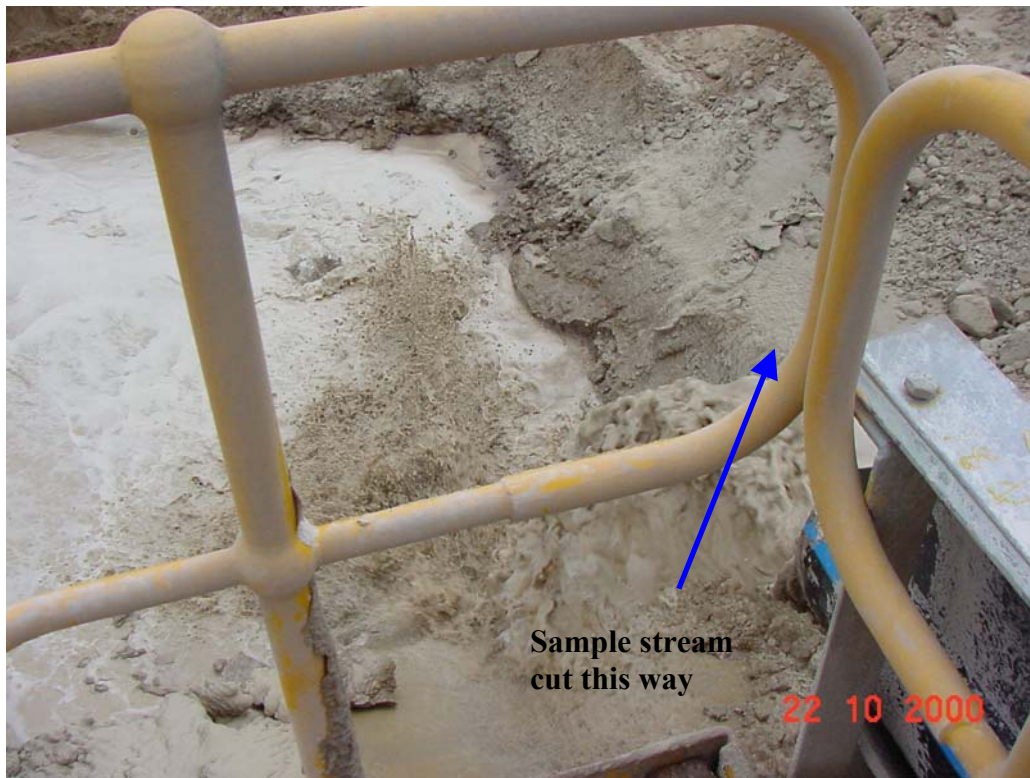

Plate 3.3. Initial sample point: PG slurry discharging from the end of the launder directly into the rim ditch.

After the first sample was taken the launder ceased to be used due to the elevation of the stack rising above that of the launder and the slurry began to be discharged through spigots into the stack pond at varying locations (Plate 3.4). However, this was an equivalent material to the first sample so the same equipment and methods were used for the rest of the sampling program.

Plate 3.4. Sampling point: spigot discharging PG slurry into rim ditch.

3.2.1 EQUIPMENT

Sample bottles were 1 litre capacity high-density polyethylene with a screw-on cap. This type of bottle would reduce the risk of spillage during transport and is impervious to the acid content of the samples, being the same material from which the stack liners are made.

The sampling scoop was manufactured on site and consists of a plastic tube scoop approximately 75mm in diameter and 20cm long glued to the end of a light-weight

wooden handle approximately 2m long. Again, this was designed for ease of use and to be impervious to acid (the scoop is also used to take daily samples of the phosphoric acid in the plant). The scoop was cleaned of residual PG in the acid process water used at the cooling tower before and after every sampling episode.

Personal protective equipment required under site regulations and as part of the requirements under the conditions of the PG stack induction included (site-wide) hard hat; long-sleeved, collared cotton shirt and long trousers; steel-capped boots; safety glasses; (PG-specific) respirator and shoulder-length acid-impervious gloves.

3.2.2   METHOD

Standing at the extreme end of the launder or next to the mouth of the spigot, the scoop is cut through the outflow with the mouth of the scoop facing in towards the flow and moving from bottom to top diagonally across the full width of the flow (Plates 3.3 and 3.4). This method was felt to give the best chance of gaining a representative sample of all particle sizes and fluids moving through the stream.

This scooping method was done twice per sample bottle, usually resulting in the sample bottle being between 60% and 80% full. It was decided not to take a third scoop as a full scoop would be too much to fill the bottle and as a result bias would be introduced into the sample, as much of the third sample would not be able to be included.

Two sample bottles were taken on each sampling occasion (approximately every four weeks, depending on the roster cycle of two weeks on/one week off) to give an increased volume of sample and help to minimise bias. Sampling continued for 12 months, to give a full seasonal profile of the material. The sample bottles were taped around the lid for extra protection from spillage and packed firmly in boxes for despatch by air to the Advanced Analytical Laboratories at James Cook University (JCU) the same morning, generally within 2 hours of being taken.   They were then analysed almost immediately upon arrival. This speed was necessary to minimise the conversion of hemihydrate (HH) to dihydrate (DH) PG.

3.3   Dihydrate Sampling

The DH samples were taken by using hand trowels to take representative samples of material from a given area on the PG stack. A clean 1.5 litre plastic container was filled with the material and delivered to the laboratory at JCU where it underwent preparation for analysis by the staff at the Advanced Analytical Centre. It should be noted that the newly deposited PG sampled for the laboratory leach columns partially liquefied during packing as it is a wetter material, having just been deposited on the side of the stack from the rim-ditch.

3.4   Hemihydrate Sampling

The HH PG was sampled using the same scoop as that for the slurry sampling. In this case it was used to cut the material falling from the overland conveyor belt into the re-slurry tank (Plate 3.5) and stored in a clean 1.5 litre plastic container for transport to the JCU laboratory. Once there it also underwent sample preparation by the laboratory staff.

Plate 3.5. Sampling point: HH PG being discharged from overland conveyor into re-slurry tank.

3.5 Dissolution Column Analyte Sampling

Two sets of columns were eventually made to test the test the dissolution of metals, metalloids, nutrients and radionuclides from unaltered PG material. Both leachate and primary material were analysed, the latter before and after the dissolution process. The first experiment failed due to weather conditions while the second was a success. Details of each are outlined below.

3.5.1 FIELD LEACH COLUMNS

The original plan for the column experiments was to replicate as closely as possible the real weather conditions that any PG fill would be exposed to. The initial experiment was designed to look only at the impact of rainfall on the PG, as this was felt at the time to be the most likely source of fluid input into any backfill. To this end large leach columns were to be set up and left in a safe location in the mine to experience real leaching during the wet season of 2001/2002. The columns were designed to withstand exposure to all weather conditions for a period of 12 months while minimising the effect of evaporation on any leachate. The columns were placed in an open area at the north-western corner of the Galah North pit, where there was good, all-weather access but it was out of the way of all traffic.

3.5.1.1 Equipment

Sixteen new 20 litre plastic buckets were obtained and 120mm diameter holes were drilled into the bottom of eight of them. All buckets were then rinsed with water and given a final acid-wash in 1 molar hydrochloric acid. 5 micron filter material was placed in the bottom of each holed bucket, sealed in place with silicone sealant, and the holed bucket placed inside a complete bucket. A plastic apron was placed around each column to prevent contamination from entering the leachate. Initially, as it was the dry season with no rain expected for many months, a second plastic container (120mm diameter, 1 litre capacity) was placed inside the outer bucket and below the drilled hole, with the inner bucket in contact with the top of the container, in order to catch any liquid drained from the PG (Figure 3.1). With the arrival of the wet season the smaller

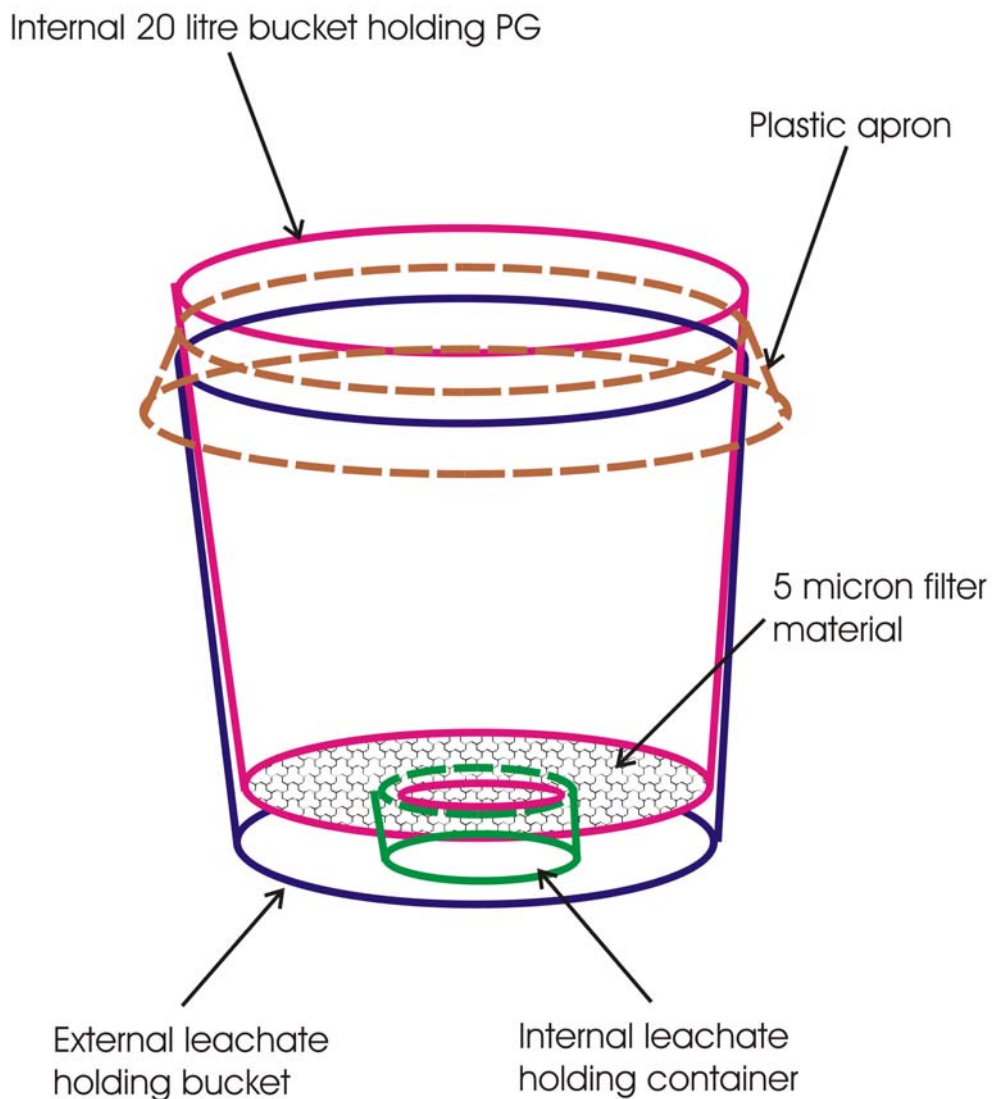plastic container was to be removed to allow for collection of the expected greater volume of leachate.

Figure 3.1 Schematic of field leach columns (not to scale).

The prepared columns (with a lid added to each and each pair enclosed in a polyethylene bag to prevent contamination during transport) were then taken to the gypsum stack where columns 1A to 1D inclusive were filled with PG from the emergency gypsum stockpile area, HH filter cake material that had been produced on Christmas Day 2000 during a failure of the agitator in the re-slurry tank. As such, it was expected to be a mixture of DH and relict unconverted HH. Columns 2A to 2D inclusive were filled with material from the north-eastern corner of the central cell which had been deposited there during the previous week (*i.e.* between 9 and 16 July

2001). Using material of two different ages and chemistry was felt to give an opportunity to study the leachate that would emerge from older *versus* newer deposits. The completed columns were then transported (under the same conditions to prevent contamination) to the experiment area where they were laid out, unlidded and barricaded off with pegs, warning tape and signs (Plate 3.6).

Plate 3.6. Field leach columns in place, Galah North pit.

3.5.1.2 Method

The leach columns were filled with approximately 20kg of PG and then left exposed to actual weather conditions at Phosphate Hill for 12 months. Any leachate was to be collected once per month and transported on ice to Townsville for analysis at the Centre for Tropical Freshwater Research at JCU.

The small container was not needed as no liquid drained from the PG. In addition, although individual monthly totals were higher than average, that particular wet season proved to be among the driest since records began in the region (on nearby Chatsworth

Station, starting in 1915), with the wet season (August 2000-July 2001) recording 196.5mm (Figure 3.2) and followed by the calendar year 2002 registering only 80mm of rain (significantly less than 236mm annual site average). What rain did fall was absorbed within the top 2cm of the PG and, as a result, there was no leachate available to be recovered.
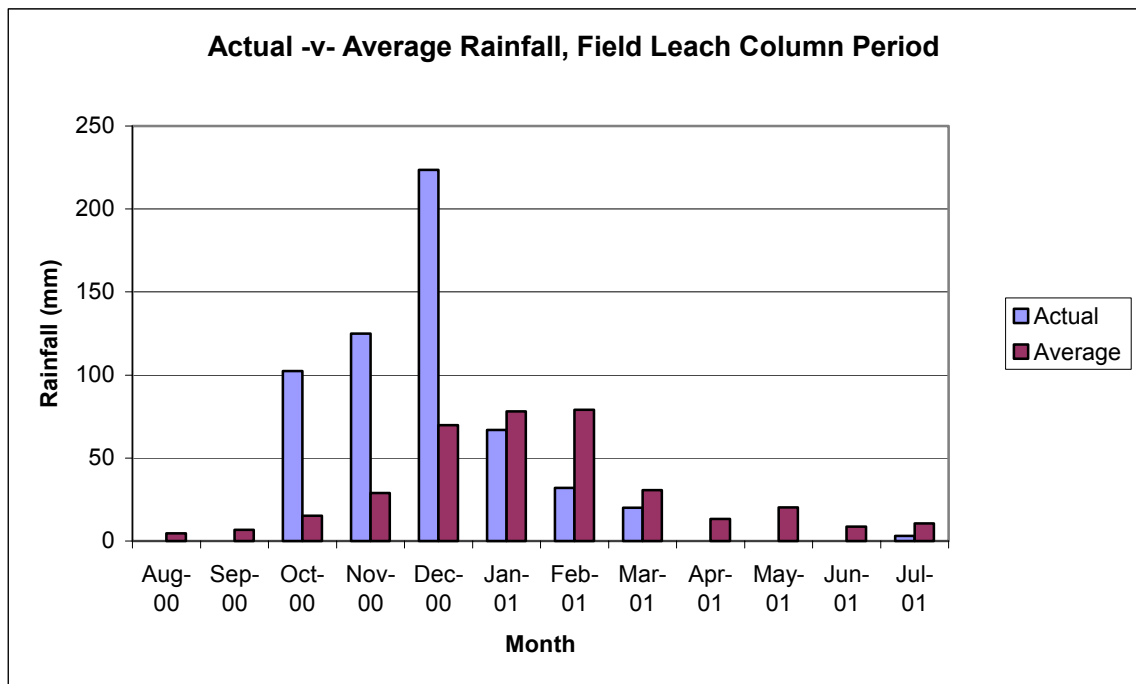

Figure 3.2. Actual *vs.* average monthly rainfall over the field leach column trial period, August 2000 to July 2001.

The field leach columns are still in place but to the time of writing (January 2004) had still not produced any leachate, despite recent higher rainfall.

3.5.2 LABORATORY DISSOLUTION COLUMNS

When it became obvious that the field experiment was going to fail, three small columns were set up in the laboratory at JCU and the contents were initially to be exposed to a minimum of one years' regional equivalent rainfall of 294ml (this figure gained by averaging the continuous historical results for Chatsworth Station, 34km east-south-east of Phosphate Hill, at 236mm/year between 1915 and 2000 and the continuous records from Mt Isa, 140km to the north, that had been combined with very sporadic Monument Village/minesite records between 1975 and 2000 to give 352mm/year). By this stage mining had begun to intersect groundwater during footwall clean-ups and

evidence of the highly transmissive nature of the aquifer was visible during those times. In addition, the possibility of complete inundation of backfilled pits by flood events needed to be considered. Galah Pit had been filled with water overflowing from Kolar Creek in 1974 in what is estimated to be a 1:2 year flood event (PPK 2000). These factors, combined with the necessity to produce at least 100ml of leachate for analysis at each flush and a desire to have the results of at least four flushing events, eventually resulted in at least 600ml of water being passed through each column during the course of the experiment.

3.5.2.1 Equipment

The columns were manufactured by Paul Givney of the Department of Earth Sciences at JCU and consisted of 20cm lengths of 50mm diameter PVC piping with 170 micron mesh glued into the base. These were set up in a custom-made varnished wooden frame which allowed a small glass beaker with a plastic funnel in the top to be placed directly below the base of the tube and removed without the need to tip the beaker (Figure 3.3). Once the leaching water was added to the column plastic cling film was wrapped around the base of the column and draped over the outside of the beaker to prevent any contaminants from entering the leachate and to minimise the possibility of evaporation during the leaching period. Paper was used to lay over the top of the columns to prevent contaminants entering the PG during and between leaching events.
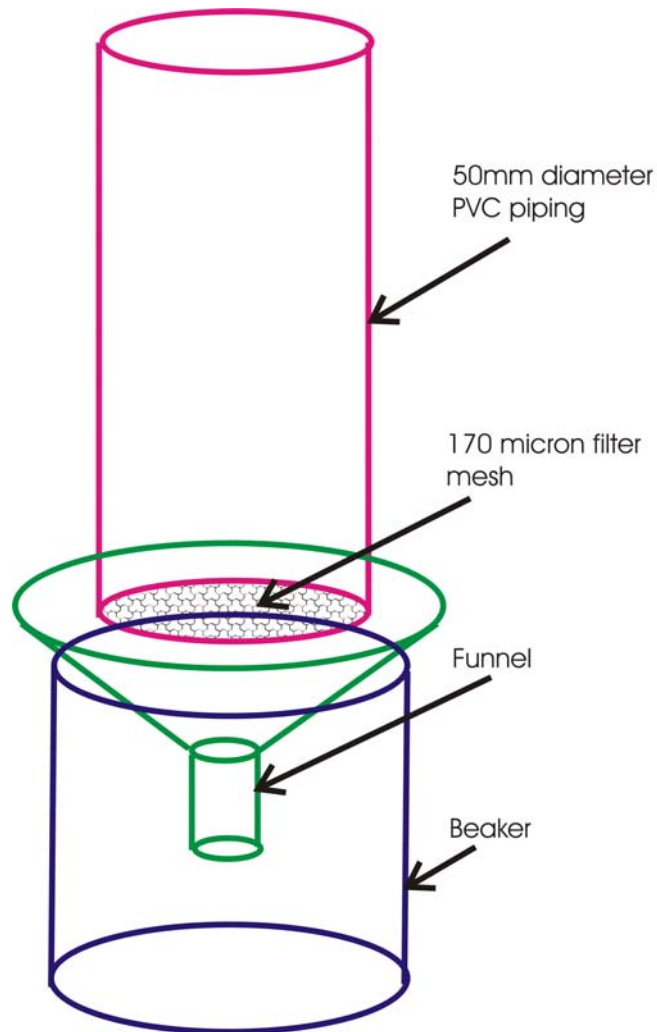
Figure 3.3 Schematic of laboratory leach columns (not to scale).

3.5.2.2 Method

Each column was loaded with 100 grams of PG: column one with HH (sample HEMI),
column two with "new" DH (GYP-N) and column three with aged DH (GYP-O). The
HH was sampled off the overland conveyor belt into the re-slurry tank and was fresh out
of the phosphoric acid plant; the GYP-N DH was sampled from an area that had seen
the solids pulled out of the PG pond within the previous few hours and so had been
pumped into the stack some time over the previous 3-5 days; and the GYP-O DH was
sampled from 3-4m below the current top of the stack and was estimated from surveyed
stack growth rates to be around 4 months old. All samples were analysed before being
loaded into the leach columns.

Dissolution took place on four to five different occasions over a period of six weeks, after which the remaining material inside the columns was re-analysed. Measured amounts of distilled water was poured into the columns and left to pass through the PG. The leachate was collected in 150ml glass beakers that had been washed in distilled water and then transferred, after measurement of the leachate volume in washed, glass measuring tubes, into new, washed 100ml polyethylene bottles and immediately transported to the laboratory for analysis. A blank consisting of 100 ml of distilled water sampled from the same supply as used for the leaching itself and the washing of the beakers/bottles was submitted with the leachate samples as a control measure. Due to the necessity of gaining a minimum of 100ml of leachate per leaching event to carry out all the analyses required, to have the results of more than two flushes to study, and to simulate the effect of complete inundation of the PG due to flooding, the amount of water passed through each for all of the leach columns totalled more than the equivalent of average annual rainfall.

3.6   Methods of Analysis

PG slurry and dry product samples were all analysed by XRF and XRD to gain results in major and trace element chemistry as well as quantitative mineralogy. The dry samples for the leach columns were also subjected to SEM analysis before leaching for both crystal morphology and chemistry. The analyte was tested for pH, conductivity, major and trace elements as well as nutrients. The following summaries of the sample preparation and analysing procedures were provided by the Advanced Analytical Laboratory and the Australian Centre for Tropical Freshwater Research, James Cook University.

Preparation of the slurry material required separation into liquid and crystalline components. For this the following method was used (Chappell 2004 *pers. comm.*):

1.   The whole sample was allowed to drain its liquid naturally.
2.   The liquid was then analysed without any further preparation apart from that required for the equipment (see section 3.6.3. below) .
3.   The solid portion was air dried and prepared as noted below in the appropriate sections.

At no time was any pressure or heating applied to the samples.

3.6.1   X-RAY FLUORESCENCE SPECTROMETRY (XRF)

Two types of X-ray Fluorescence were carried out on the samples, semi-quantitative XRF and quantitative XRF. For both methods the samples were dried at 40°C and then prepared into pellets or fused beads, as appropriate. A variety of commercial and in-house standards were used for the calibration of the machines. The commersial standards were GYP-D, GBW03109, GBW03111 and SDO-1. Several in-house standards (GYP1-GYP9) were also manufactured from high-purity chemicals in order to replicate the composition of the Phosphate Hill PG, which does not match any commercial gypsum standard. Details of the chemistry and reproducibility of these standards is contained in Appendix 10. Fusion temperatures were kept to 1100°C to prevent loss of fluoride.

3.6.1.1 Semi-quantitative X-ray Fluorescence Spectrometry

Five grams of each sample was crushed and pressed into a powder pellet. The samples were then analysed in a Siemens SRS 3000 XRF Spectrometer. The data collected from the various scan ranges (covering from C to U) were processed using Siemens Semi-Quant Software (SSQ) to give indicative values for the sample chemistry.

3.6.1.2 Quantitative X-ray Fluorescence Spectrometry

For this method 0.34 grams of each sample was crushed and mixed with a Lithium Borate flux and fused at 1100ºC to make the glass disc suitable for XRF analysis. The samples were then analysed using a Siemens SRS 3000 XRF Spectrometer. The data collected from various scan ranges were compared to existing calibrations based on international standards.

3.6.2   POWDER X-RAY DIFFRACTION (XRD)

An agate mortar and pestle was used to lightly crush approximately 0.5 grams of sample. This was then packed into a plastic cavity mount suitable for insertion into the X-ray Diffractometer.   Equipment used was a Siemens D500 front-loading X-ray Diffractometer fitted with a copper tube (Cu Kα = 1.54178 angstroms), operating at 40kV and 30 mA, and a post diffraction graphite monochromator.   The sample was scanned from 1.3º 2Θ to 65º 2Θ in steps of 0.2º 2Θ for 2.4 seconds per step. Analysis was done using standard procedures and the SIROQUANT XRD software package which uses the full-profile Rietveld method of refining the profile of the calculated XRD pattern against the profile of the measured XRD pattern.   The total calculated pattern is the sum of the calculated patterns of the individual patterns and the results are compared to the international ICDD database. Quartz was used as an internal standard. Accuracy is ±1%. There is no precision scan available for this method.

XRD is inherently not an accurate and precise quantitative method due to factors that affect the output. These include the particle size, orientation of the phases, variability of the chemistry and crystallinity of the sample.   The quality of the scans can also be affected by such factors as sample preparation, data collection settings and instrument conditions. Limitations of these analyses were noted as follows:

a.   The limit of detection on most minerals is 1-2%, rising to 5% for high-iron bearing minerals.

b.   Overlap of diffracted reflections can occur where multiple mineral phases exist, resulting in some ambiguity in interpretation.

c.   Mineral phases present in minor or trace amounts cannot be unambiguously identified. These include, in this study, the amphibole and the clays.

Errors on the analyses are as follows, and are absolute (Ness *pers. comm.* 2004):

       0-10%   ±2%

       10-50%   ±5%

       50-100%   ±10%

The technique should not be regarded as an absolute quantification but rather as an indicator of relative trends.

3.6.3   INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICPMS) AND ATOMIC EMISSION SPECTROMETRY (ICPAES)

Preparations for liquid sample analyses via ICP saw the original liquid sample passed through a 0.45μm Millipore filter and then diluted 10-fold using 1% HNO_3 following the procedure USEPA200.8, with 100ppb Rh added into the samples, blanks and calibration standards for use as an internal standard for trace element analysis.   An initial semi-quantitative panoramic scan was performed for all elements except Fe using ICPMS on a Varian UltraMass 700 to identify the elements present in the samples. Thereafter, the identified elements were divided into trace and major element groupings.

Trace elements were determined using ICPMS (as above) with a series of multi-element standard solutions used as the external standard for instrument calibration.   Major elements, including Fe, were determined using Inductively Coupled Plasma Atomic Emission Spectometry (ICPAES) on a Varian Liberty Series II machine, with a determination limit of 0.5ppm.   As with the trace elements, a series of multi-element standard solutions purchased from a reputable commercial source were used for the external calibration of both ICPMS and ICPAES and Ga and In were used as an internal standard on the former to correct for matrix effects and instrument drift.   ICPMS results with high concentrations were checked using ICPAES.

3.6.4   PARTICLE SIZING

The slurry was sampled for particle size using a Malvern Mastersizer-X laser particle size analyser.   For this the dried PG was passed through a 1mm sieve to remove large particles.   The sieved sample was checked for grain segregation and a random sub-sample of 3mm^3 taken using a spatula.

This sub-sample was then dispersed in water and treated with ultrasound for 20 seconds prior to analysis in order to disaggregate any clumps.   The sample was then strongly agitated before being passed through the particle size analyser.   Sizing was then

conducted using 10000 sweeps of the detector, a 1000mm lens, to detect particles between 1.8 and 2000 microns. The laser diffraction data was then processed using Malvern software to produce the particle size distribution in 32 size classes.

3.6.5   SCANNING ELECTRON MICROSCOPE (SEM)

The initial samples analysed by SEM (leach column material) were dried and mounted onto Al stubs while the later samples (metal phase examination) were dried and cast as a resin block which was then cut to provide a cross-section and the surface polished. The samples were then carbon coated to provide an electrically conductive surface. The initial samples were analysed using a JEOL JXA840A electron probe microanalyser operating at an accelerating voltage of 15kV while the later samples were studied in a JEOL JXA 8200 EPMA also operating at 15kV acceleration. They were initially examined using backscatter electron mode to determine overall homogeneity and then energy dispersive spectrometry was used to perform elemental analyses.

3.6.6   ANALYTE CHEMISTRY

The leach column analyte was assessed for pH and conductivity, major and trace elements and total Phosphorous, filterable reactive phosphorous (FRP) and silica. This was done using standard procedures (*e.g.* Persulfate digestion for total P) as appropriate on an Alpkem Autoanalyser utilising segmented flow.

3.6.7   RADIONUCLIDES

Samples of PG slurry were taken from the spigot outflow on Cell 4 during October 2003 and despatched to the Australian Nuclear Science and Technology Organisation (ANSTO) at Lucas Heights for analysis. ANSTO had previously completed a study in 2000 (Brown *et al.* 2000) which looked at radionuclide behaviour throughout the processing stream at Phosphate Hill, from the raw material in the mine to the fertilizer and PG products and including samples of scale and the contents of the slimes dams.

For the recent sampling study, three one-litre plastic bottles were filled using the method described above in s.3.1 and shipped *via* air freight to ANSTO. On arrival the

three samples were combined and then filtered to separate liquid from solid and to provide the required >1kg of crystalline material for radon emanation tests. The solids were not washed (to maintain field conditions) and were dried at 40ºC before pulverising and subsampling for the analyses. Both slurry and solids were analysed for U-238, Ra-226, Pb-210 and Po-210 using the ANSTO in-house procedure ENV-I-029-002 "Radiochemical Analysis for U, Th, Pb and Po". An aqua regia technique was used to digest the solids with U-238, Pb-210 and Po-210 then separated using ferric hydroxide as a co-precipitate. Solvent extraction was used to separate the Pb-210 and Po-210 after dissolution of the precipitate in HCl whilst the U-238 was separated *via* ion exchange. Alpha-spectrometry was used for Po-210 and U-238 and beta spectrometry for Pb-210. Ra-226 was co-precipitated with lead sulphate and ultimately counted using alpha spectrometry.

Determination of radon exhalation from the solids was *via* ANSTO in-house procedure ENV-I-031-006 "Determination of Radon Progeny Concentrations in Mixed Phase Samples by Gamma Spectrometry". The sample was oven dried and crushed to <1mm. It was then sealed in a Marinelli beaker and counted using a high purity germanium crystal gamma detector. After 30 days storage the sample was re-counted and the difference between the two results used to determine the radon emanation coefficient and the exhalation rate.

3.7   Sampling Objectives

There are four components of the PG system that required analysis. These are the hemihydrate filter cake that comes from the initial acidulation process; the "new" dihydrate solids that are released from the re-slurry tank into the sedimentation pond on the top of the PG stack; the "old" dihydrate that occurs after the completion of the hemihydrate-dihydrate conversion process and represents the long-term material available from the stack; and the acid return process water that is drained from the stack and used in the re-slurry process. All of these components required analysis as there are several options for in-pit disposal:

(a)   as hemihydrate directly off the filter belts;
(b)   as a slurry;

(c)   as filtered dihydrate; or

(d)   as aged, rehandled material from the existing stacks.

The slurry was sampled over a 12 month period. This was in order to examine any variations in the product due to seasonal conditions or changes to the sources of the ore (pits) being processed. It also covered a major shut-down and re-start of the entire fertilizer plant. Each monthly sample of the slurry consisted of two bottles of material to act as field duplicates.

It was also necessary to sample the leachate derived from the various types of PG in order to assess its potential environmental impact. Leachate was initially planned to be obtained under conditions as close as possible to those actually existing in the field to gain a realistic result. However, one of the driest wet-seasons on record saw the original attempt abandoned in favour of more traditional laboratory conditions. In addition to testing the leachate, the PG material used in the columns was analysed both before and after leaching, using the same methodologies employed for the base-line testing.

Differing analytical methods were used as appropriate to the material being scrutinised. These followed standard testing procedures and were carried out by appropriately qualified and experienced personnel at the Advanced Analytical Centre and the Australian Centre for Tropical Freshwater Research at James Cook University and at ANSTO in Sydney. The results will be presented in Chapter 4.