THE EVOLUTION OF PASSIVE MINE WATER TREATMENT TECHNOLOGY FOR SULPHATE REMOVAL

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ABSTRACT

A sustained 14-year major research effort has been undertaken in South Africa to develop integrated passive water treatment systems for the sustainable removal of sulphates under acidic, neutral and alkaline conditions, while simultaneously addressing the removal of metals and acidity. The research effort addressed the problem both at a fundamental science level and at the more empirical pilot plant level. Whereas there are numerous anaerobic sulphate reducing reactors in operation on mine waters that remove some sulphate together with metals and acidity, these are typically plagued by low sulphate removal efficiency and gradual reductions in overall reactor efficiency with time.

A key feature of a successful passive sulphate reduction technology is the need to also develop a passive sulphide oxidation technology that is capable of removing the sulphides produced from sulphate reduction before they can be reoxidised back to sulphate. Additionally, conventional anaerobic sulphate reduction technology has encountered a lower pH limit of 4.5, below which the reactors cease to function effectively. This lower limit has also been breached through a sustained research effort and a bioneutralization technology, based on sulphate reduction, has also been developed that can successfully treat highly acidic mine water at pH values as low as 2.8 and containing over 1000 mg/l of metal acidity.

This paper presents the evolution of this research over the last 14 years and also sketches the current status of the various passive treatment technologies that have been developed.

1. INTRODUCTION

The global mining industry is increasingly facing challenges regarding the sustainable long-term treatment of mine effluents, in some cases for decades after the closure of the mine. While a variety of active treatment technologies are available to treat practically any type of mine water, such active technology typically has the disadvantages of higher cost (capital and operating costs), a higher degree of supervision and operator attendance, reliance on external power requirements such as electricity and in certain developing countries, high risk of theft of valuable plant components, either resulting in system failure or in the need for expensive round-the-clock security systems.

Passive water treatment technology has a key role to play in the treatment of contaminated mine waters that typically contain elevated levels of acidity, metals and sulphates. While there are different types of passive treatment technology available to the design engineer, such as anoxic limestone drains (ALD), successive alkalinity producing systems (SAPS), constructed wetlands, oxidation ponds, etc., research in South Africa has been heavily focused on the development of passive anaerobic sulphate reduction technology (Pulles, et al, 2003).

A sustained 14-year major research effort has been undertaken in South Africa to develop integrated passive water treatment systems for the sustainable removal of sulphates under acidic, neutral and alkaline conditions, while simultaneously addressing the removal of metals and acidity. The research effort addressed the problem both at a fundamental science level and at the more empirical pilot plant level. Whereas there are numerous anaerobic sulphate reducing reactors in operation around the world on mine waters that remove some sulphate together with metals and acidity, these are typically plagued by low sulphate removal efficiency and gradual reductions in overall reactor efficiency with time. While the technology developed in South Africa is able to operate at high sulphate reduction rates of between 1700 and 9200 mmol.m^{-3}.d^{-1}, the technology has typically encountered a lower pH operating limit of around pH 4.5.

A key feature of a successful passive sulphate reduction technology is the need to also develop a passive sulphide oxidation technology that is capable of removing the sulphides produced from sulphate reduction before they can be re-oxidised back to sulphate. Additionally, conventional anaerobic sulphate reduction technology has encountered a lower pH limit of 4.5, below which the reactors cease to function effectively.

As many mine waters are in the strongly acidic range of pH 2.5 – 4.5, a research programme was launched in South Africa in 2003 to develop a passive bio-neutralization technology capable of treating acidic mine waters with a pH < 3 and containing over 1000 mg/l of metal acidity. The reactor configuration used for the research was the patented Degrading Packed Bed Reactor (DPBR) previously developed in South Africa for the high rate passive removal of sulphates. For this purpose, passive treatment is defined as follows:

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A water treatment system that utilises naturally available energy sources such as topographical gradient, microbial metabolic energy, photosynthesis and chemical energy and requires regular but infrequent maintenance to operate successfully over its design life. A major, sustained 14-year research programme has been undertaken by Pulles Howard & de Lange Incorporated (PHD), Golder Associates Africa (GAA) and various other research institutions, with funding from various agencies, including the South African government (Department of Arts Culture, Science and Technology's Innovation Fund), the Water Research Commission, Anglocoal, BHP Billiton, Eskom and most of the major coal and gold mining groups in South Africa (Pulles et al. 2003). This research commenced in 1995 and went through three major and distinct phases, resulting in the registration of a first patent application in 2001 (Pulles & Rose, 2001). Further work after patent registration has focused on the development of the bio-neutralization technology, development of the sulphide oxidation technology and the full-scale demonstration of the DPBR technology. All these developments are summarized in this paper.

2. BACKGROUND TO THE PASSIVE SULPHATE REDUCTION PROCESS

The biological reduction of sulphate to sulphide, using an organic carbon source as the electron donor, is the process upon which the passive sulphate reduction technology rests. This process is used in both active and passive technology configurations, with the primary distinguishing feature of the passive technology being that the carbon source takes the form of a solid lignocellulose. This lignocellulose may be provided in various forms, including manure, straw, hay, sewage sludge, wood chips and a variety of agricultural solid residues.

While there are different ways of constructing the chemical equation for the biological degradation of lignocellulose in the reduction of sulphate, a useful one is the following:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{-2} = 53HS^- + 67HCO_3^- + 39CO_2(aq) + 39H_2O + 16NH_4^+ + HPO_4^{-2}$$

The above equation is a simplified one, as the actual process within a biological reactor is a complex step-wise one, where the solid lignocellulose is first hydrolysed and solubilised, whereafter it is progressively fermented to simpler organic compounds which can ultimately be utilized by the sulphate reducing bacteria. Previous work (Pulles et al, 2003) undertaken in South Africa clearly showed that the hydrolysis of the complex lignocellulose was undoubtedly the rate-limiting step in a passive sulphate reducing reactor.

While this insight might seem trivial, a prior review of the literature on passive sulphate reduction suggests that many researchers were not aware of this phenomenon as the literature abounds with optimistic results for passive sulphate reduction, derived from relatively short-term laboratory studies. The many long-term reactor studies undertaken by PHD and GAA clearly indicated a common time-related performance trend for passive sulphate reduction reactors, typified by the performance curve shown in Figure 1 below.
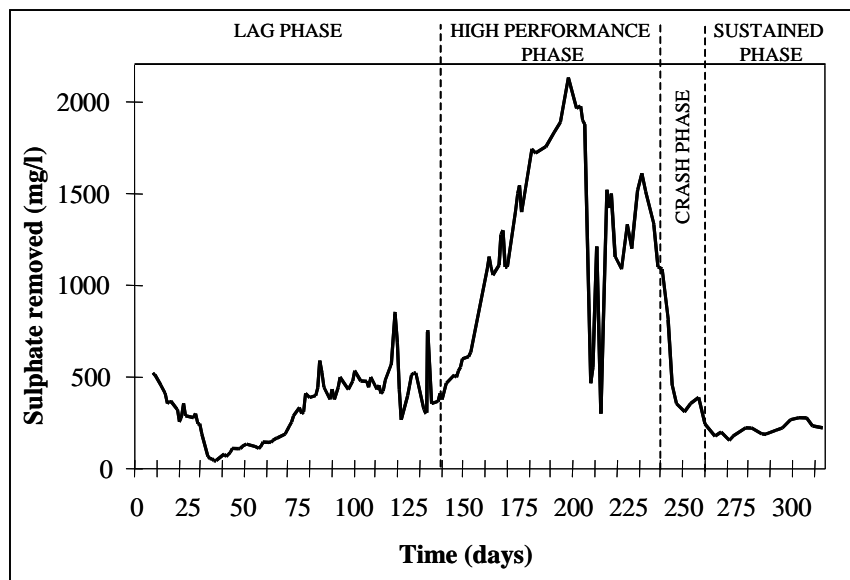

Figure 1. Typical sulphate reduction performance for passive reactor

The curve shown in Figure 1 is typical of a standard passive sulphate reduction reactor with regard to the following performance phases:

1. A lag phase with a typical duration of around 90 days (closer to 150 days in the case of Figure 1) during which time the reactor bacterial populations are adapting to the environment and sulphate reduction is relatively low.

2. A very efficient high performance sulphate reduction phase, typically not lasting longer than 8 months after reactor startup, during which time the readily available and hydrolysable energy in the lignocellulose

is very efficiently utilized in sulphate reduction.

3. A sharp decline or crash in reactor performance, typically in the 8th or 9th month after reactor startup, resulting from the exhaustion of the readily hydrolysable lignocellulose. The onset of this phase may be retarded if the reactor is operating at excessively long hydraulic retention times.

4. A sustained but sharply reduced rate of sulphate reduction that will last for a period of 5 to 6 years if no replenishment of lignocellulose occurs.

5. Eventual cessation of sulphate reduction capability due to inability to hydrolyse the remaining lignocellulose material

Phases 1 to 3 have been observed numerous times in the hundreds of reactor studies undertaken by PHD and GAA over the 14 year period from 1995 to 2009. Phases 4 and 5 have been observed in long-term field pilot scale studies undertaken by PHD at the Vryheid Coronation Colliery in Kwazulu-Natal, South Africa. The monitoring programme at this pilot plant was undertaken over a 10-year period from 1996 to 2006. With more than 1 million data points, this pilot plant is undoubtedly the world's best monitored passive sulphate removal plant and has revealed very valuable information about the long-term performance of these reactors. This research is being written up in the form of a research report to be published early in 2010 by the Water Research Commission.

Much of the research published in the literature is for studies that have not been undertaken for long enough to move through the crash phase into the low level sustained sulphate reduction phase and the results of such research should be used with caution and should not ever be used to inform reactor design exercises. Based on our research, we have found that the typical low level sustained sulphate reduction rate will be of the order of 300 millimoles per cubic metre per day (300 mM/m^3/d) with lower levels being obtained if hydraulic short-circuiting is prevalent. This corresponds well with results reported in the PIRAMID Consortium report (2003):

Tentative design values for SO_4^{2-} removal in such systems range from 300 millimoles per cubic metre per day (mM/m^3/d) (Gusek, 1998; Lamb et al., 1998) to approximately 800 mM/m^3/d (Willow and Cohen, 1998).

It is not clear whether the value of 800 mM/m^3/d reported in the above extract from the PIRAMID report refers to data obtained from the high performance Phase 3 of the reactor or for the low level sustained sulphate reduction found in Phase 4.

It is furthermore relevant to note that the research that has been undertaken suggests that the energy contained within a lignocellulose carbon source can be divided into the following components:

- Firstly, there is the readily soluble fraction that is typically mobilised and washed out of the reactor within the first 2 weeks. This fraction comes available when the reactor is still in its lag phase and gives rise to the initial reasonable sulphate reduction performance within the first 2-3 weeks of the reactor. However, a large fraction of this energy is lost and the passive reactor typically exhibits a very high COD load in the first 2 weeks.

- Secondly, there is the readily hydrolysable fraction that requires bacterial population adjustment during the lag phase and is then subsequently utilized during the high performance sulphate reduction in Phase 2 to drive high rates of sulphate reduction. Sulphate reduction values in excess of 7000 mM/m^3/d have been repeatedly observed. The exhaustion of this fraction of the lignocellulose is dramatically shown by the crash in reactor performance at around the 8th month of operation.

- Thirdly, there is the difficult to hydrolyse fraction that represents the bulk of the energy contained within the lignocellulose. This fraction represents the cellulose and hemicellulose that is protected by the lignin biopolymer that coats the lignocellulose fibres. This energy is partially available in a standard passive sulphate reduction reactor and will support a sulphate reduction rate of 300 mM/m^3/d for a period of 5-6 years. Based on research undertaken by PHD it has been shown that a standard passive sulphate reduction reactor will not mobilise all the potential energy represented by this fraction.

- Fourthly, there is the recalcitrant energy fraction which is simply not available to biological metabolic pathways but which would be released using aggressive chemical, physical and/or thermal action.

- Finally, there is the ash fraction that represents the non-reactive portion of the lignocellulose.

- The real challenge in obtaining high rate passive sulphate reduction is in finding ways of liberating the difficult to hydrolyse fraction at a higher rate than 300 mM/m^3/d and at a high conversion efficiency where the bulk of this fraction is utilized and only the fourth and fifth lignocellulose fractions are left.

3. DEVELOPMENT OF THE NOVEL PASSIVE TREATMENT TECHNOLOGY

This realization that passive sulphate reduction reactors were constrained by lignocellulose hydrolysis rates led to the initiation of an in-depth research programme to find ways of overcoming this rate-limiting step, thereby unlocking the energy available within the lignocellulose for sulphate reduction, at a rate high enough to make the technology economically viable (originally set at >600 mM/m^3/d). This research pursued the following two different paths:

- Pretreatment (aerobic) of the lignocellulose to make the lignocellulose less resistant to anaerobic bacterial action.

- Understanding of the mechanisms of anaerobic lignocellulose hydrolysis in order to develop a process that could optimize this step.

The first leg of the research was undertaken in collaboration with the University of Pretoria and involved the fungal degradation of lignocellulose material. The objective of this research was to use various white rot fungi to weaken the lignin structure before the lignocellulose was packed into the anaerobic reactors, thereby affording the anaerobic bacteria better access to the cellulose and hemicellulose fractions. An offshoot of this research was an investigation into the utilization of the concentrated organic liquor leaching from the fungal reactors as an energy source in the sulphate reduction process. This leg of the research, while showing technical promise, was ultimately terminated on the basis of preliminary economic evaluations that indicated that even using best case data, the costs of such a process would far outweigh the benefits.

The second leg of the research was undertaken in collaboration with the Environmental Biotechnology Research Unit at Rhodes University. This leg of the research was successful and the understanding obtained from this research led to the development of a novel reactor called the Degrading Packed Bed Reactor (DPBR) that was designed to optimize the hydrolysis of lignocellulose. This concept is novel insofar as the primary design and operating purpose of the reactor is lignocellulose degradation as opposed to sulphate reduction. The performance of the DPBR is measured not only in the rate of sulphate reduction, which is exceptionally high for a passive reactor, but also in the ability to produce an effluent high in organic loading (measured as COD) to be utilized in subsequent sulphate reducing reactors.

In terms of the typical passive sulphate reduction performance curve shown in Figure 1, the effect of overcoming the lignocellulose hydrolysis rate-limiting step is to significantly reduce the effect of the crash phase and to lift the sustained sulphate reduction phase to a higher level than the default 300 mM/m^3/d efficiency found in a standard passive reactor.

The outcome of the research is the development and patenting of a new integrated and managed passive treatment process, known as the IMPI Process. The essence of the IMPI process is the subdivision of the overall treatment process into individual units, each designed and optimized to perform a key function. This integrated process is shown in Figure 2 below.
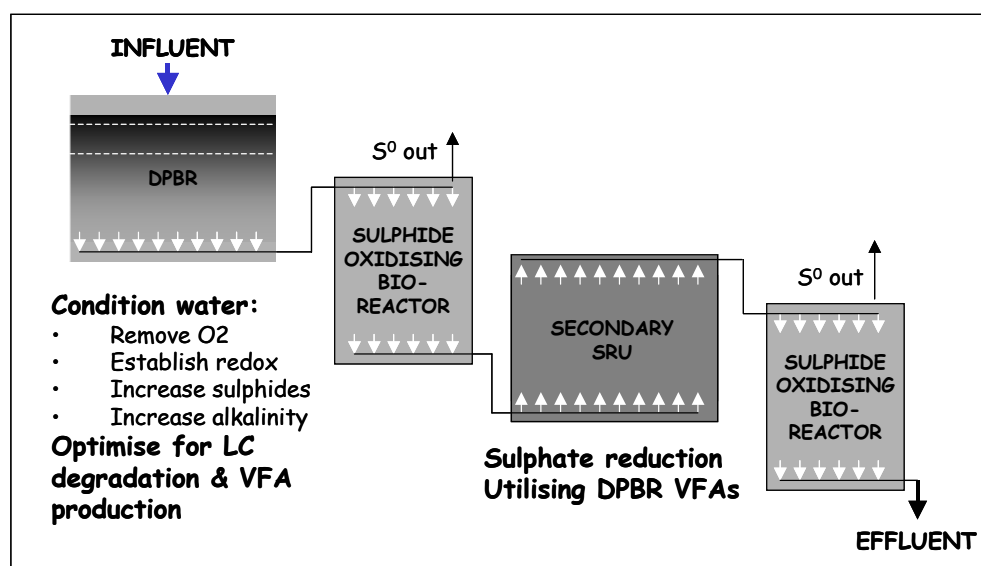

Figure 2. Schematic of the IMPI process

The purpose and essential features of the 4 different stages can be summarised as follows:

Reactor 1: Degrading Packed Bed Reactor (DPBR): This reactor is packed with multiple layers of specially selected carbon sources (electron donors) and also receives regular inputs of readily available carbon. The primary functions of this unit are to rapidly condition the influent by removing dissolved oxygen, establishing the desired redox conditions and producing elevated levels of sulphides and alkalinity in the first portion of the reactor. The remainder of the reactor is devoted to the optimized hydrolysis of lignocellulose material and the production of volatile fatty acids (VFA). The effluent from this reactor will contain reduced levels of metals and sulphate and elevated levels of sulphides, alkalinity, VFAs and nutrients.

Reactor 2: Primary Sulphide Oxidising Bioreactor (PSOB): This reactor contains no carbon source and has the primary function of oxidizing sulphides to elemental sulphur for removal from the reactor while minimizing changes to the VFAs, nutrients and redox conditions and preventing full oxidation of sulphides back to sulphates.

Reactor 3: Secondary Sulphate Reducing Reactor (SSRR): This reactor contains a specially selected selection of carbon sources. The primary function of this reactor is to utilize the VFAs produced in the DPBR and to remove additional sulphate down to the design level. The effluent from this reactor would contain reduced levels of metals, sulphate, VFAs and nutrients and elevated levels of sulphides, and alkalinity.

Reactor 4: Secondary Sulphide Oxidising Bioreactor (SSOB): This reactor contains no carbon source and has the primary function of oxidizing sulphides to elemental sulphur for removal from the reactor.

If required, a final aerobic polishing stage could be added, primarily to remove residual levels of VFAs and nutrients. The individual units could be combined in a tapered –up or tapered-down configuration, i.e. one DPBR to many SSRRs or vice-versa, depending on the design duty of the reactors.

A typical data set showing the long-term performance of a DPBR reactor with regards to sulphate removal is given in Figure 3 below.
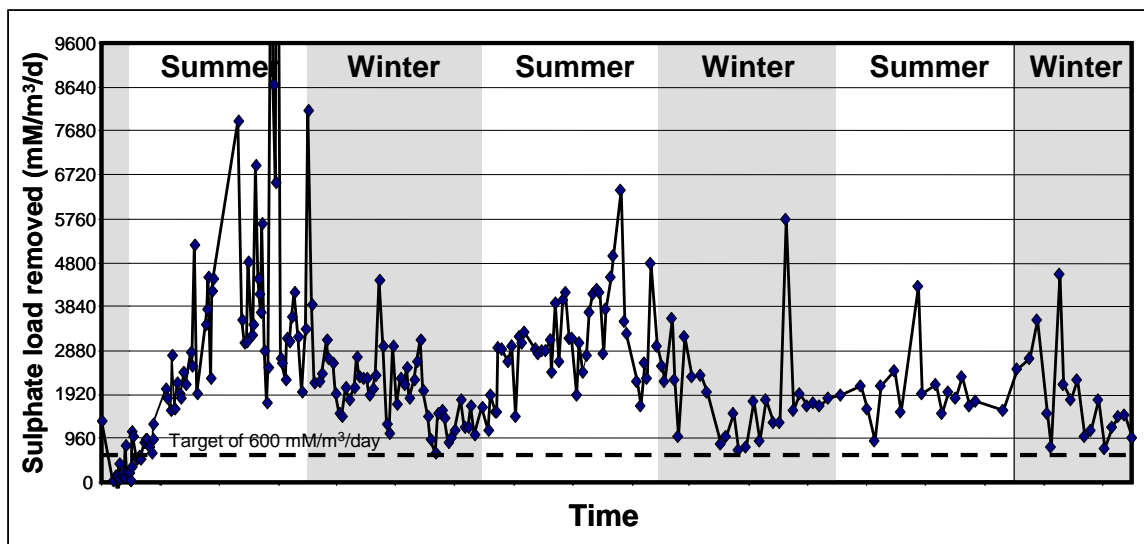

Figure 3. Extended DPBR Performance Results

The data presented in Figure 3 does indicate that the DPBR is able to sustain the long term sulphate reduction or removal rate at or above 2000 mM/m^3/d, representing a 7-fold increase in performance over the standard sulphate reduction reactor with a removal rate of around 300 mM/m^3/d. Figure 3 also indicates that the removal efficiency fluctuates with the winter and summer seasons and that there is a gradual decrease in the removal rate due to the consumption of the lignocellulose material. The operating strategy for a DPBR is therefore to incorporate an annual replenishment of lignocellulose material to replace the fraction that has been consumed. While this has not been applied to the reactor depicted in Figure 3, this action can be expected to exert an upward force on the performance curve to counteract the gradual decline.

Figure 4 presents sulphate removal (in mg/l), alkalinity production and sulphide production data for the same long-term DPBR reported in Figure 3. Figure 4 shows a much more marked seasonal effect on alkalinity production than on sulphate reduction or sulphide production. It is also of interest to note that the reactor effluent sulphide concentrations do not exceed 400 mg/l and are more typically at around 300 mg/l, suggesting that the maximum sulphate reduction that can occur in a single stage passive sulphate reduction reactor is around 900 to 1000 mg/l sulphate.
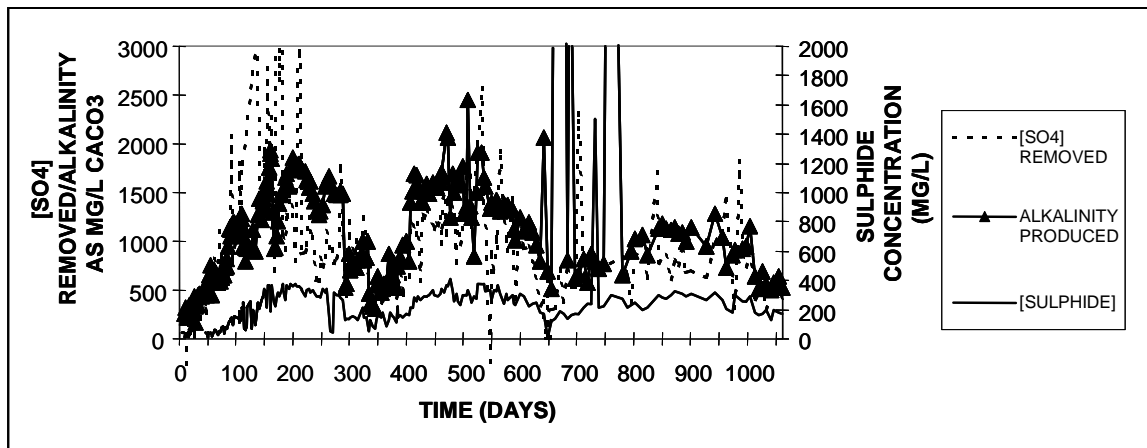
Figure 4. Long-term performance of DPBR in terms of sulphate concentration removed,
alkalinity produced and sulphide produced

4. IMPLEMENTATION OF THE IMPI TECHNOLOGY

While the research programme has resulted in the development of a detailed descriptive process model that serves as the basis for plant and process design, the implementation of the technology needs to take account of various site-specific factors. The treatment process is a biological one and therefore needs to be customized to take account of unique site conditions, specifically the following:

1. Each mine water has a unique chemistry that affects the biological process design and the commissioning and operating procedures.

2. The technology requires a large inventory of carbon substrate on initial construction and each site will have a unique blend of carbon substrate that is sourced as close as possible to the plant.

3. Each site has unique physical features that affect the civil construction and the available hydraulic driving head.

In order to address these uncertainties, a standardized 4-phase implementation procedure has been developed that ensures that the above factors are fully defined and incorporated into the existing descriptive process model in order to produce an optimized site-specific plant design. This procedure is shown schematically in Figure 5 below.
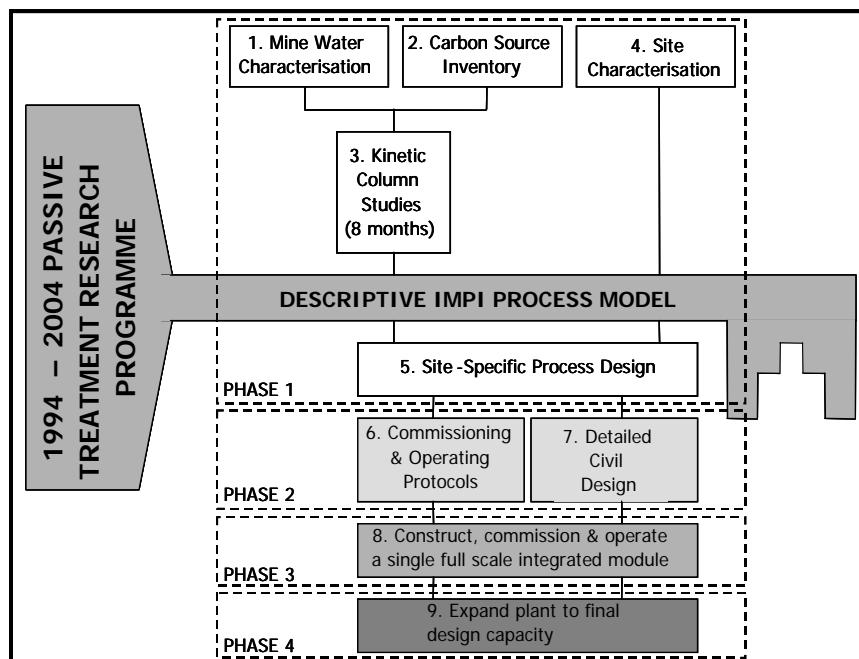

Figure 5. Implementation procedure for IMPI passive treatment technology

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Phase 1: Develop Site-Specific Process Design Parameters

Step 1: Obtain all historical water quality records and any information that may exist on predicted future water qualities for the anticipated design life of the plant. Evaluate these data in order to obtain a current and possibly future characterisation of the water to be treated. Establish and confirm the desired treatment objectives, i.e. which contaminants need to be removed and to what levels? Define the design treatment duty of the passive treatment plant.

Step 2: Based on the existing descriptive process model, undertake a first-order conceptual process design in order to establish a first estimate of the volume of carbon required as an initial inventory. Undertake a survey to establish potential carbon sources within a 25km radius of the proposed plant location and obtain representative samples of this carbon material. Undertake batch anaerobic evaluations of the carbon samples and compare to the carbon source performance database in order to obtain a ranking of carbon source suitability. Select a carbon mix or suite of mixes, to be utilized in the kinetic column studies as being representative of the desirable carbon mix for a full-scale passive treatment plant.

Step 3: Undertake kinetic passive treatment column evaluations in the passive treatment laboratory using the carbon mix selected in Step 2 and using the actual mine water to be treated. In order to customize the descriptive IMPI process model to optimally treat the actual mine water under investigation, a set of 8 columns is operated for a period of 36 weeks. The experimental programme that is applied to these reactors is aimed at establishing performance criteria specific to the mine water and carbon mix at the site. It is not appropriate to undertake such experimental work on full-scale modules that each contain 1000 m^3 or more of carbon substrate and the column reactors are used for this purpose. A 36-week test period is required to overcome the initial 60-90 day commissioning period and to generate sufficient data to enable extrapolation over a 20-year design life.

The experimental programme also develops the specific commissioning and operating procedures that may be required to ensure satisfactory treatment of difficult-to-treat mine waters. As part of the experimental programme, analyses of influent and effluent are undertaken for sulphate, sulphide, COD, alkalinity, pH, redox potential, iron, aluminium and manganese.

Step 4: Undertake site evaluations in order to establish potential physical locations for the proposed passive treatment plant components. These site evaluations include establishment of the following data:

- Obtain record of flow rates of water to be treated, including information on peak flow conditions.

- Establish available static hydraulic head on the water to be treated and establish practical limits to increasing this head.

- Obtain a site survey plan accurate to 0.5m contour levels for the selected potential site.

- Establish relevant floodlines and plot them onto the site survey plan.

- Excavate test pits down to 4-5m in order to establish ground conditions. Subject soil samples to suitable laboratory tests to determine structural and hydraulic properties.

- Prepare a scoping EIA report regarding the suitability of the proposed site for construction of a passive treatment plant.

Step 5: Utilise the data generated in Steps 1-4 in order to develop a site-specific process design that can be used as the basis for a detailed civil engineering design for the full-scale plant. This site-specific process design is fundamentally based on the descriptive IMPI process model that then incorporates inputs from Steps 1-4 described above to ensure that it is optimized in terms of the actual mine water to be treated and the actual carbon substrates to be used.

Phase 2: Detailed Civil Design, Commissioning & Operating Protocols

Step 6: Based on the column studies undertaken as part of Step 4, the site-specific commissioning and operating protocols are defined and appropriate commissioning and operating manuals are prepared. These protocols / manuals also document the management, monitoring and auditing requirements for the particular plant.

Step 7: Based on the process design prepared in Step 5, and taking account of the developed commissioning and operating protocols, a detailed civil engineering design is prepared. The design is based on the construction of a single full-scale integrated module, although all water distribution and collection systems are designed with the objective of future addition of modules (Phase 4) to handle the full flow of water to be treated. Drawings and tender enquiry documents are developed to enable tenders to be sought for the actual plant construction and for subsequent plant commissioning and operation. This step also includes the completion of a proper EIA with the necessary water use licences to enable the plant to be constructed and operated.

Phase 3: Construct Single Full-Scale Integrated Module

Step 8: Once the construction tender has been awarded, construction work is undertaken to construct the plant in accordance with the civil design. Construction work needs to be closely supervised to ensure that work meets the specifications and that static commissioning objectives are met. Once construction has been completed, full wet commissioning commences – this commissioning may take as long as 90 days. The commissioning phase will also be used to ensure that the operating contractor is fully trained to adequately operate the plant. Once the plant is deemed fully commissioned, it will revert to the standard operational sequence and the appointed operating contractor will assume his/her operational duties. It is envisaged that Phase 3 would typically have a duration of 12-18 months before moving to Phase 4.

Phase 4: Expand Plant to Final Design Capacity

Step 9: Once the operation of the single full-scale module has proceeded satisfactorily for a period of 12-18 months, a decision can be made to expand the plant (i.e. construct additional parallel full-scale modules) to treat the full mine water flow. The performance of the single operating full-scale module will be reviewed and, if necessary, the process design prepared in Step 5 will be reviewed and modified. Steps 6, 7 and 8 will then be redone for the additional full-scale modules.

To date, Phase 1 performance or amenability studies have been undertaken on 7 different coal mine effluents – 3 in the Witbank coalfields in the Mpumalanga province and 4 in the Vryheid coalfield in the KwaZulu Natal province. Typical datasets deriving from such a study are shown in Figures 6 and 7 below.
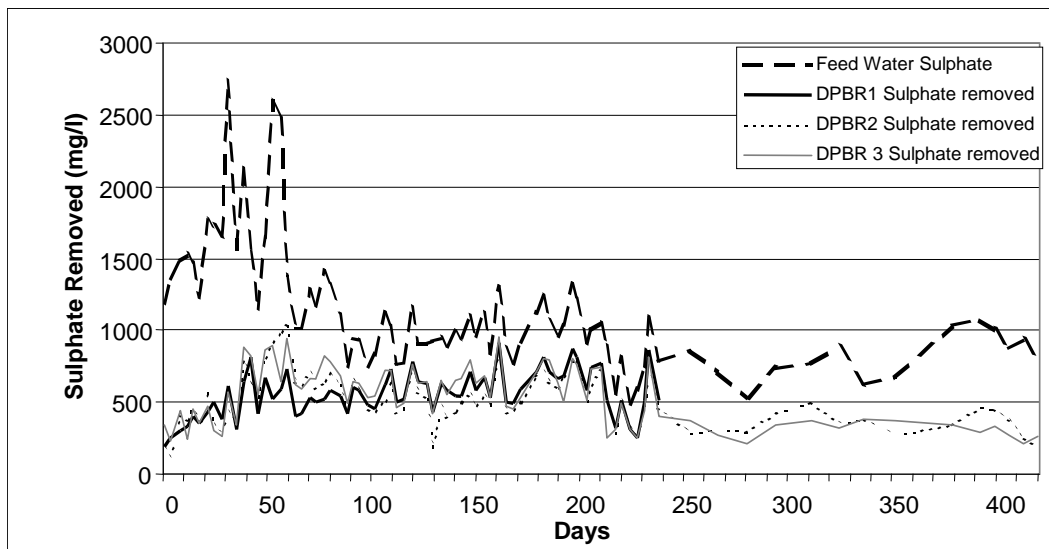

Figure 6. Design studies for a South African colliery – sulphate concentration removed
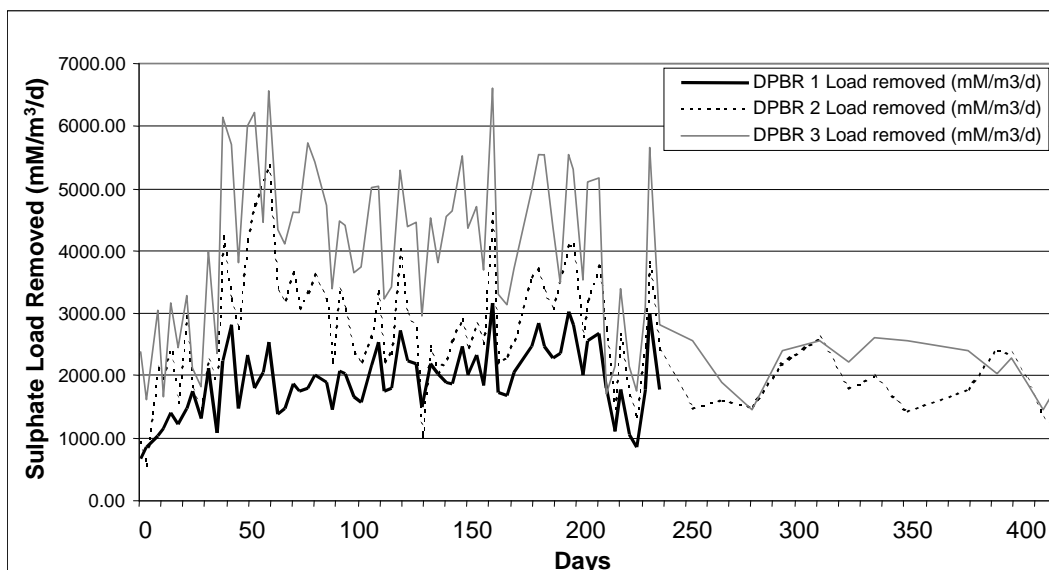

Figure 7. Design studies for a South African colliery – sulphate load removed

A project is currently being implemented by the South African coal mining industry to construct and operate a single 200 m³/day full-scale module at a Mpumalanga Colliery and to evaluate its field performance for a period of 18 months – this equates to Phase 3 as shown in Figure 5.

5. CONSTRUCTION AND EVALUATION OF FULL-SCALE DPBR REACTOR

One of the 7 mines for which the Phase 1 studies were undertaken (as shown in Figures 6 and 7 above) was used to take the technology further into Phases 2 and 3 (refer to Figure 5 to see phases). This project has been underway for some time and is being funded mainly by the mine involved in terms of capital and primary costs, but also collectively by most of the coal mining companies in South Africa through the Coaltech 2020 research programme. The current status of this project is that the plant has been constructed and is currently undergoing commissioning, with detailed evaluation planned for the remainder of 2009, 2010 and the first half of 2011.

This plant consists of the following components (refer to Figures 2 & 8 and Plates 1 & 2):

- 200 m³/day Degrading Packed Bed Reactor (DPBR)
- 20 m³/day Primary Sulphide Oxidation Reactor (PSOR)
- 20 m³/day Secondary Sulphate Reducing Reactor (SSRR)
- 20 m³/day Oxidation Cascade
- 20 m³/day Aerobic Wetland

The objectives of this project are as follows:

1. Evaluate the field performance of a single full-scale module of the new DPBR at 200 m³/day in order to determine its suitability for full-scale construction and operation.

2. Evaluate an experimental 20 m³/day PSOR in parallel with a smaller laboratory-scale PSOR in Golder Associates Research Laboratories in order to evaluate and optimize process operating conditions under field conditions.

3. Evaluate an experimental 20 m³/day SSRR in order to demonstrate the integrated series process of DPBR to PSOR to SSRR.
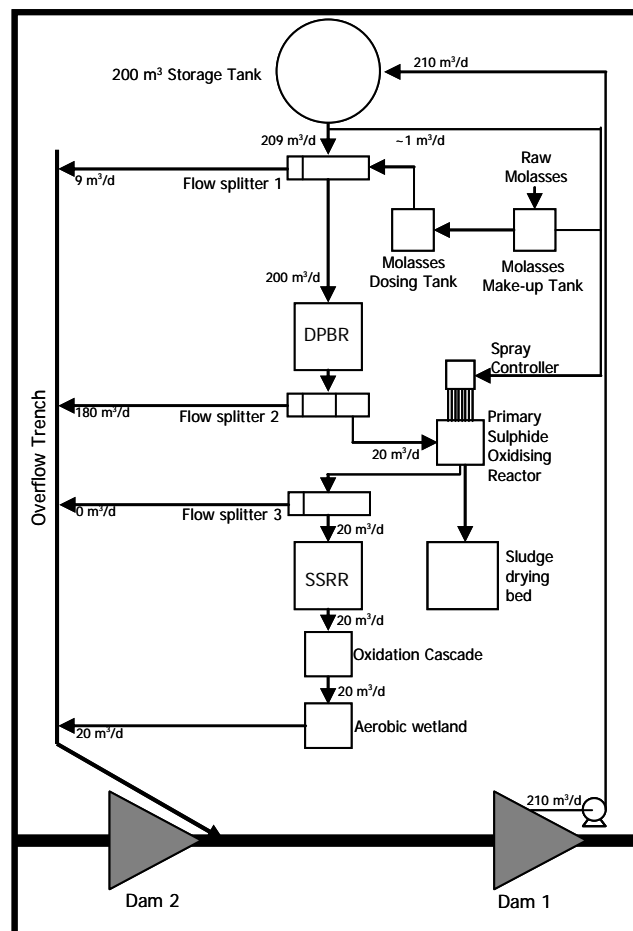

Figure 8. Schematic Layout of Prototype IMPI Plant

Plate 1. View of Prototype Plant   Plate 2. Filling of DPBR with Carbon

6. DEVELOPMENT OF A PASSIVE BIO-NEUTRALIZATION TECHNOLOGY

Conventional anaerobic sulphate reduction technology, including the standard DPBR, has encountered a lower pH limit of 4.5, below which the reactors cease to function effectively. This lower limit has also been breached through a sustained research effort and a bio-neutralization technology, based on sulphate reduction, has also been developed that can successfully treat highly acidic mine water at pH values as low as 2.8 and containing over 1000 mg/l of metal acidity. Bacterial populations were isolated from mine effluents and selectively cultured over a period of around 150 days to produce populations that have subsequently been used in a six-year research programme from 2003 to the present to develop the bio-neutralization technology. A detailed descriptive model of the bio-neutralization technology was developed using results from the following investigations:

- 6 years of operational results and data
- A number of depth profile studies to track reaction progression along the column
- A molecular microbial ecology study of the system
- Studies on metalliferous and highly acidic water

Using the data referred to above, the following observations were made:

1. Alkalinity generation is clearly linked to biological sulphate reduction and this can be seen by the close linkage between datasets for alkalinity generation, sulphide generation and sulphate reduction. Furthermore, the microbial ecology study has demonstrated the presence of SRBs and associated bacterial populations that have previously been isolated from acidic, anaerobic, lignocellulose-degrading environments.

2. Previous literature on acidophilic sulphate reducing systems have suggested that neutral-charged, small organic compounds are used as the nutrient source rather than organic acids. Microbial ecology studies have demonstrated the presence of a complex consortium of microorganisms involved in the degradation of lignocellulose compounds relating to acidic, anaerobic environments such as sphagnum peat bogs, Phragmites rhizosphere, wetland sediments and acidic root zones. It is significant that together with these, Clostridium species have been found that were previously isolated from the gut of termites and are likely to be involved in the fermentation of sugars and acids into neutral compounds such as alcohols, including methanol and glycerol. Microbial ecology studies have shown the presence of the various elements of the consortium needed to effect the abovementioned sequence of reactions.

3. Both the SRB and the cellulose degrading and fermenting microorganisms require substantially reducing environments and operate at low redox. It is evident that facultative anaerobes need to be present to purge residual oxygen and to poise redox conditions to below -250 mV in order for sulphate reduction to occur effectively under the highly acidic conditions. Microbial ecology studies have also shown the presence of facultative anaerobes such as Cytofaga and others closely related to facultative anaerobic metabolic forms. The presence of these organisms indicates that the molasses feed provides the nutrient source for rapid respiratory removal of dissolved oxygen and poising of redox to below -250 mV.

4. In addition to the above, it is evident from chemical analyses, that in addition to proton acidity, a substantial metal acidity contributes to the overall low pH of the system. The formation of metal hydroxides and metal sulphides contributes to both reduction of metal acidity but also to alkalinity consumption, thus exerting a complex effect on the bioneutralization reaction.

5. An unexpected observation of the depth profile studies (chemical and microbial) indicated that, in stable operating columns, the complete reaction was taking place in the first functional part of the column (200 mm of the available 2000 mm) with the rest of the column not appearing to play any useful role in the neutralization function. However, it should be noted that with system perturbation, the additional portion of the

reactor column may play a stabilizing function in managing feed fluctuations and process upsets. This observation suggests a tight spatial relationship between the three components of the biological system, namely

- Redox poising

- Production of simple carbon substrate

- Sulphate reduction

Based on the above information that has been gleaned from the various studies, together with more recent studies on acclimatizing this system to metal-rich water, the following model may be proposed:

1. Population 1: Acts to remove oxygen from the system and is composed of facultative anaerobes that can scavenge residual oxygen and rapidly reduce redox to -250 to -350 mV in the presence of high H^+ concentrations.

2. Population 2: Poising of redox enables anaerobic degradation of lignocellulose structures to simple, charge-neutral carbon compounds by a number of organisms, including Clostridium spp.

3. Population 3: SRBs that, in the presence of poised redox, can utilize the charge-neutral carbon compounds as electron donors for the reduction of sulphate to sulphide and bicarbonate, where the generation of bicarbonate and sulphide both contribute to the increased alkalinity observed in the process. Although no observations were made to support the presence of feedback loops, it is probable that the increased alkalinity and elevated pH may exercise a feedback effect on populations 1 and 2, relieving the stress of functioning at low pH conditions.

The tightly constrained spatial location of these three components of the reaction contrast sharply with the previous studies undertaken on the distribution of microbial structural functional relationships in the DPBR which occurred in linearly sequential zones along the length of the reactor. This suggests that feedback influences between the various components of the populations are critical to the operation of the system and account for the absence of a spatial distribution of the populations within the reactor.

These results suggest that the selection of highly adapted organisms and their both rapid and joint establishment to function simultaneously within the column, provides a rational basis from which to pursue a structured approach to process development.

The research undertaken over the last 6 years on the bio-neutralization technology initially focused on simply treating highly acidic waters (pH 2.5 – 3.0) but with relatively low metal concentrations. This was followed by a second major research programme on highly acidic mine waters with very high metal concentrations too – iron >1000 mg/l; aluminum > 100 mg/l; and manganese around 50 mg/l. The high metal concentrations have also required the development of additional techniques to prevent hydraulic clogging of the reactors with metal precipitates.

Results of the longest running bio-neutralization reactors, in terms of effect on pH, for the full 6-year evaluation period are shown in Figure 9 below.
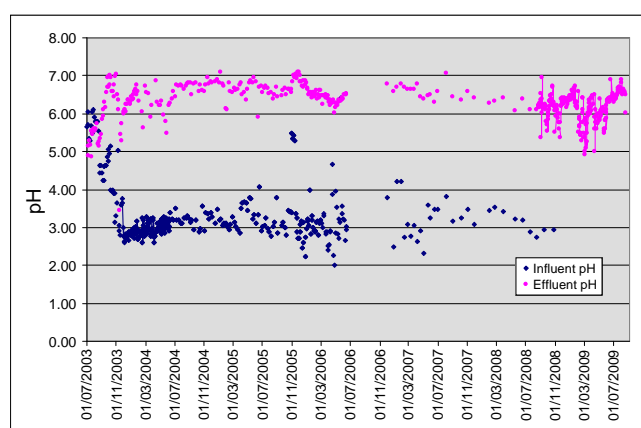

Figure 9. Results of Bio-neutralization Reactors in Terms of pH

Based on the results obtained during the 6-year research programme, the following key observations can be made:

1. Reactors need to be based on the patented DPBR technology, although reactors can be much shallower at around 1 metre effective depth.

2. Reactors only perform effectively when reactor redox potential is maintainedat levels of -300mV or lower.

3. Reactors are negatively affected by temperatures below about 15 ºC and are therefore not suitable for very cold

climates.

4. Reactors are capable of accumulating metals to values in excess of 1 kg/m^3 carbon before metals start to break through and cause reactor performance problems. However, strategies have been investigated to remove metals, allowing up to 90% recovery of removed iron but only 20% of removed aluminium.

5. Reactors are capable of removing up to 1000 mg/l sulphates in the process of effecting bio-neutralization.

6. Bioneutralization reactors can be operated in series ahead of a DPBR, allowing for effective high-rate passive sulphate reduction of highly acidic mine effluents

7. DEVELOPMENT OF A PASSIVE SULPHIDE OXIDATION TECHNOLOGY

A key feature of a successful passive sulphate reduction technology is the need to also develop a passive sulphide oxidation technology that is capable of removing the sulphides produced from sulphate reduction before they can be re-oxidised back to sulphate. Without a passive sulphide oxidation technology, it is not possible to implement passive sulphate removal systems.

The removal of sulphide from acid mine drainage (AMD) treated effluent particularly in passive treatment has been a subject of interest at Pulles Howard & de Lange (PHD) and Golder Associates Africa (GAA). Preliminary studies were carried out jointly between PHD and Environmental Biotechnology Research Unit (EBRU), Rhodes University as part of an Innovation Fund passive treatment project. The results of these studies indicated that biological sulphide oxidation has potential for the removal of sulphide from passive AMD treatment systems such as integrated managed passive (IMPI) treatment systems. This resulted in the award of Water Research Commission (WRC) funding during 2002 for the development and refinement of the floating sulphur biofilm reactor. Subsequently, a three year project funded by the WRC was carried out at EBRU with GAA forming part of the steering committee. This study focused on fundamental investigations of the molecular microbial ecology, structural, functional and chemical characteristics of the floating sulphur biofilm reactor under controlled environment. As an output of this project, the linear flow channel reactor was developed and operated under controlled conditions. Results of this study have accounted for 65% sulphide removal - 56% of which was recovered as sulphur.

A scale-up of the linear flow channel reactor for removal of sulphide from the passive IMPI system has been included as part of the passive demonstration plant to be built at a colliery and discussed in Section 5 of this paper. However, the reactor developed in the EBRU study, is currently not robust enough to be operated as part of the demonstration plant and a parallel research project is being undertaken with WRC funding through which optimisation of the pilot-scale reactor on the demo plant will be carried out. This research unit would feed into the pilot-scale reactor and various operational parameters will be optimised in the laboratory studies before being implemented on the demonstration plant. This technology is referred to as the Linear Flow Channel Reactor.

The purpose of the linear flow sulphide oxidation reactor is to convert the sulphide rich effluent from a degrading packed bed reactor (DPBR) into elemental sulphur. The sulphur biofilm technology has been demonstrated under laboratory conditions with various levels of success, as discussed in Molwantwa *et al.* (2007). The purpose of the demonstration field unit is to test the technology under field conditions as well as to test various process configurations and thereby refine the full-scale design parameters. In order to achieve this, the reactor has been built with as much flexibility as possible, while keeping the reactor as simple as possible.

The objective of the reactor is for the floating biofilm to oxidise the sulphide to elemental sulphur while limiting the oxidation back to sulphate and achieving near complete removal of sulphide from the feed water. The sulphur formed needs to be harvested from the biofilm at intervals ranging from 6 to 18 hours, depending on the thickness of accumulated sulphur in the biofilm, with a typical ideal interval of 12 hours. Channel compartments are harvested one at a time so that there are always sufficient sections of the reactor that have an active oxidising biofilm to remove the sulphide. The harvested sulphur will accumulate at the bottom of the channels until the depth of accumulated sulphur requires that the channels be cleaned. See Plates 3 and 4.

Plate 3. Sulphur Biofilm being Harvested   Plate 4. Harvetsed & Dried Solid Sulphur

The technology being investigated and refined in current research projects stems from research programmes that commenced more than a decade ago and that have progressively evolved to the current status.

8. CONCLUSIONS

The research programme into the development of an integrated passive treatment system for sulphate removal from mine waters has been a sustained effort undertaken over a period of 14 years from 1995 to 2009 and additional evaluations and research are still continuing. We have seen progressive improvement in the performance of the system as the research has gone through the different phases.

1. The research programme has led to the following novel developments in passive treatment technology:

2. The Degrading Packed Bed Reactor capable of sustained high rate sulphate reduction at rates around 700% higher than other published rates.

3. Bio-neutralization technology capable of extending the passive sulphate reduction to mine waters with pH values as low as pH 2 and containing metals in excess of 1000 mg/l.

4. Sulphide oxidation technology that promises to be an effective component of an integrated passive treatment system and which can linearise the sulphur cycle to produce elemental sulphur that can be extracted from the water.

5. Full-scale field demonstration of the technology currently being initiated.

The technology developed during this research project is firmly based on two major South African biological sulphate reduction research initiatives. The first initiative has been ongoing for a period of around 15 years by Pulles Howard & de Lange and subsequently Golder Associates Africa and has focused on passive sulphate removal technology. The second initiative has been ongoing for a period of around 15 years by the Environmental Biotechnology Research Unit at Rhodes University. These two initiatives started off operating independently but have been cooperating with true synergy for the last 10 years. The collective manpower investment in these two initiatives is believed to be of the order of 120 man years and the collective budget in 2009 value would exceed R100 million. The leading position occupied by South African researchers in the field of passive sulphate removal technology is therefore not accidental, but is rather the product of a sustained and concerted research effort and a sustained support from the South African research funding agencies and South African mining industry.

9. ACKNOWLEDGEMENTS

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