

COMPARISON OF THE MMS CN-D™ CYANIDE DESTRUCTION PROCESS WITH CARO'S ACID, SMBS/AIR AND HYDROGEN PEROXIDE OPTIONS

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ABSTRACT

Modern gold plants are under increasing pressure to adopt world-class cyanide management practices due to escalating environmental pressures, particularly for signatories to the International Cyanide Management Code. Operations are lowering the levels of weak-acid dissociable (WAD) cyanide reporting to spigot discharge and to any eventual discharges from the tailings storage facility (TSF). Gold operations are increasingly adopting the inclusion of cyanide oxidation processes into their circuits, particularly for greenfields projects. These processes predominantly use sodium meta-bisulfite (SMBS, or SO_2) with air, Caro's acid (H_2SO_5), or hydrogen peroxide (H_2O_2).

Maelgwyn Mineral Services (MMS) has developed the MMS CN-D™ process, which utilizes the Aachen Reactor™, a high-energy mass-transfer superoxygenation system, in conjunction with an activated carbon-based catalyst, to increase the rate of cyanide oxidation to cyanate, the thermodynamically more stable form. These four processes are compared with respect to stoichiometric reagent costs, chemical reaction efficiencies and risks, as well as logistical, operability, safety and environmental issues, for both remote sites and those close to urban areas. Considerable potential upside benefit is demonstrated for MMS CN-D™ compared with the alternative cyanide destruction processes. Additional potential features of the MMS CN-D™ process are also considered, such as the potential to recover additional gold otherwise lost to tailings, to de-risk implementation and lower capital costs via staged integration of Aachen Reactors™ into existing oxygenation and SO_2 /Air equipment and to modify existing plant tankage in CIL trains to become part of the MMS CN-D™ cyanide destruction plant component.

Finally, the current development and commercial status of the MMS CN-D™ process is described. A brief overview is also given of recent pilot-scale and bench-scale testwork conducted at the Maelgwyn Australia testwork facility in Perth Australia. The MMS CN-D™ Process is shown to have considerable potential qualitative upside in comparison to the three most common oxidative cyanide destruction process routes. Oxidative reagent transportation, storage, mixing, dosing and safe handling are clear potential issues for the SMBS/Air, Caro's acid and peroxide processes. Environmental issues such as elevated salt and sulphate loads due to sulphur addition, as well as the risk of corrosive contamination of wildlife habitats on overdosing excursions, are additional factors to be considered when implementing conventional chemical dosing cyanide destruction methods. These factors become particularly important in both remote sites and sites located close to urban areas.

From the reagent cost model outputs for a nominally typical gold plant requiring a comparison of the four options considered in this paper, it is concluded that costs for the Caro's acid route are higher than the other routes; this effect is substantially magnified in the case of the sulphide ore (300 mg/L SCN) as compared with the oxide ore (0 mg/L SCN). SMBS/Air and hydrogen peroxide routes report somewhat reduced reagent costs. MMS CN-D™ reagent costs are significantly lower than those of the other three cyanide destruction process routes considered.

Additional upside potential exists in the case of the MMS CN-D™ Process, given that additional gold leaching is expected in some cases, due to mineral surface cleaning in the high-shear cavitation zone of the Aachen Reactor™, along with enhanced gold adsorption equilibrium onto the CN-D™ carbon, subject to carbon movement. Significant bench and pilot-scale testwork has been completed. The first full-scale MMS CN-D™ plant has been constructed at a gold plant in East Africa and is currently awaiting CIP plant stabilization and commissioning.

INTRODUCTION

Modern gold plants are under increasing pressure to adopt world-class cyanide management practices due to escalating environmental pressures, particularly for signatories to the International Cyanide Management Code, who require their operations to reduce levels of weak-acid dissociable cyanide (WADCN) reporting to spigot discharge to tailings storage facility (TSF), typically to <50 mg/L, as discussed by Gibbons [1]. Gold operations are increasingly adopting the inclusion of cyanide oxidation processes into their circuits, particularly for greenfields projects. These processes predominantly use sodium meta-bisulfite (SMBS, or SO_2) with air, Caro's acid (H_2SO_5), or hydrogen peroxide (H_2O_2). These oxidizing reagents are corrosive and present an additional hazard regarding the transportation, storage and usage of these expensive reagents. Moreover, additional environmental issues have been associated with these routes – increased salt and sulphate loads to the environment, and overdosing can produce corrosive effluents in wildlife habitats.

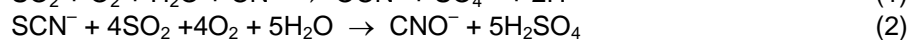
Maelgwyn Mineral Services (MMS) has developed the patented MMS CN-D™ process [2], which utilizes the Aachen Reactor™, a high-energy mass-transfer superoxygenation system, in conjunction with an activated carbon-based catalyst, to increase the rate of cyanide oxidation to cyanate, the thermodynamically more stable form. These four processes are compared in this paper with respect to stoichiometric reagent costs, chemical reaction efficiencies and risks, as well as logistical, operability, safety and environmental issues, for both remote sites and those close to urban areas.

Cyanide Destruction Processes for Gold Plant tailings

It is well known that a wide range of cyanide complexes of different stabilities are formed with metals including Au, Ag, Cu, Ni, Fe, Zn, Co commonly found in gold plant solutions. Moreover, cyanide in both bound and free states can be oxidized to the cyanate ion (OCN^-) and ultimately to carbon dioxide and nitrogen.

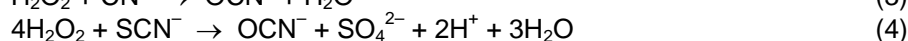
These oxidation reactions are constrained by their relatively slow rates as well as the low oxygen solubility in water, even with the use of various oxygen spargers found in some carbon-in-pulp (CIP) circuits [3-5]. Modern cyanide detoxification circuits therefore typically employ chemical oxidation processes [6], such as the SO_2 /Air process, the peroxide (H_2O_2) process, and the Caro's acid (H_2SO_5) process.

The SO_2 /Air process, originally developed by DeVuyst and co-workers [7] uses air or oxygen sparging along with either gaseous SO_2 sparging or addition of chemical forms of the active form, such as sodium meta-bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) or sodium sulfite (Na_2SO_3), along with copper (II) sulfate as catalyst if insufficient copper is present in solution. The reactions depicted in Equations (1) and (2) apply:



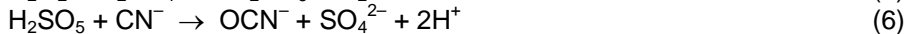
The theoretical usage of SO_2 in the process is 2.46 g of SO_2 per gram of CN^- oxidized, but in practice, usage of 3.5-5.0 g SO_2 per gram of cyanide oxidized is typical [6].

The peroxide process (described by Mathre and DeVries [8]) uses addition of H_2O_2 , along with copper (II) sulfate as catalyst if insufficient copper is present in solution. The relevant chemical reactions are depicted in Equations (3) and (4):



The theoretical usage of H_2O_2 in the process is 1.31 g of H_2O_2 per gram of CN^- oxidized, but in practice, usage of 2.0-8.0 g SO_2 per gram of cyanide oxidized is typical, due to side reactions with other solution constituents and degradation of the reagent.

The Caro's acid process (patented by Griffiths, et al [9]), uses addition of peroxymonosulfuric acid (H_2SO_5 , known as Caro's acid). The formation, cyanide and thiocyanate oxidation chemical reactions are depicted in Equations (5), (6) and (7), respectively:



Caro's acid is produced on-site by the reaction of concentrated hydrogen peroxide and sulfuric acid in a controlled environment with an overall product yield of up to 80%. Caro's acid is relatively unstable, particularly at elevated temperature, and hence must be used immediately.

The theoretical usage of H_2SO_5 in the process is 4.39 g of H_2SO_5 per gram of CN^- oxidized, but in practice, usage of 5.0-15.0 g H_2SO_5 per gram of cyanide oxidized is typical, due to side reactions with other solution constituents, particularly thiocyanate (SCN^-), and degradation of the reagent. Acid produced in the reaction is typically neutralized with lime, if necessary. The oxidation reaction proceeds without the need for a soluble copper catalyst.

MMS CN-D™ Cyanide Destruction Process

The MMS CN-D™ Cyanide Destruction Process [2] utilizes the Aachen Reactor™. This concept for mineral slurry reactors originated in Germany, and was originally developed in the 1970s for applications in flotation. The Aachen Reactor™ is designed to improve gas-liquid mass transfer using energy provided in pipeline flow. The fundamental principle is the use either of a slot aerator or a micro-fine gas diffuser made from high-tech, non-blinding materials in a high velocity flowstream. Additionally, a secondary chamber provides regeneration of bubble surfaces using various hydrodynamic effects.

The objective is to increase utilisation of the gas phase, thus reducing overall energy and reagent costs. The reactor contains no moving parts, and is designed to withstand erosive effects of mineral slurries. Materials of construction can be selected according to application. Commercial applications were recently described by Flatman, et al [10] and include the Aachen™-assisted leaching of gold ores with cyanide and high-rate oxidation of sulphides (Leachox™ Process). The reactor accelerates the slurry or solution stream at the gas addition point and increases shear rates in the subsequent flow mixing zone. The reactor has been designed to maximise the phase interface surface area at this point in the mixing zone by means of a proprietary gas diffusion system which generates extremely fine gas bubbles. The total pressure, under which the unit operates, can be selected according to the requirements of the process. As schematically depicted in Figure 1, the Aachen Reactors™ consist of (i) a novel bubble generation system made from advanced materials, and (ii) pressure/after-mixing/cavitation chambers that effectively force the micro-bubbles into solution, and that do not coalesce or flash off.

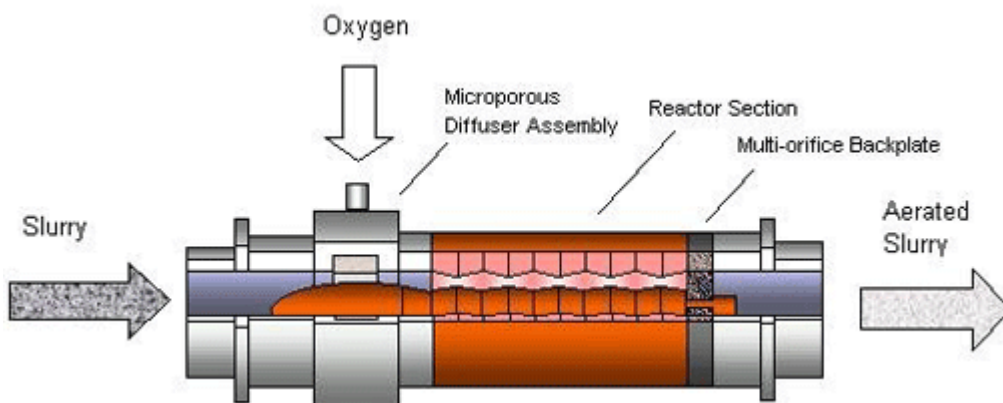
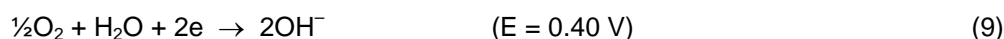
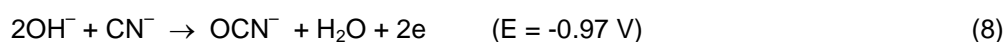


Figure 1: Aachen Reactor™ for superoxygenation of slurries in the MMS CN-D™ Process

The resultant super-oxygenated solution contains extremely high DO levels and is subsequently passed into contact with an activated carbon-containing tank. In this stage the carbon acts as a catalyst for the oxidation of cyanide and in combination with the super-oxygenation extent achieved via the Aachen Reactor™ ensures the rapid oxidation of cyanide to benign cyanate and carbonate species, as depicted in Equations [8-11]:



QUALITATIVE COMPARISON OF CYANIDE DESTRUCTION PROCESSES

The four cyanide destruction processes under consideration in this paper are compared with regard to several conceptual qualitative factors in Table 1. These factors should be considered in conjunction with cyanide speciation chemistry of the solution to be treated, the CIP plant configuration and the indicative reagent cost comparison summarized below.

Table1: Conceptual Comparison of Qualitative Risk Factors in Cyanide Destruction Processes

Process	Logistical	Operability	Safety	Environmental
MMS CN-D™	Potential to utilize existing tankage, carbon & O ₂ dosing	Low wear; low blockage rate; pump maintenance	Oxygen handling	None
SMBS/Air	Multistage tanks, dosing & reagent handling	Precision liquid/gas/slurry mixing system; dosing pump maintenance	Corrosive chemical; toxic SO ₂ gas on hydrolysis	Elevated salt load; corrosive to wildlife on overdose; reagent transport
Caro's Acid	Multistage tanks, dosing & reagent handling	Precision mixing & reagent preparation system; dosing pump maintenance	Corrosive & acidic chemicals	Elevated salt load; corrosive to wildlife on overdose; reagent transport
Peroxide	Multistage tanks, dosing & reagent handling	Precision dosing system & pump maintenance	Corrosive chemicals	Corrosive to wildlife on overdose; reagent transport

Reagent transportation issues are compounded when remote sites are involved, while safety and environmental issues become broader and more visual for sites located close to urban areas.

REAGENT COST COMPARISON OF CYANIDE DESTRUCTION PROCESSES

The four cyanide destruction processes under consideration in this paper are compared with regard to conceptual estimated reagent costs, which are typically a major operating cost component. Full operating and capital cost estimation is beyond the scope of the present study.

Cost Model Inputs

A simple cost model was set up based on a nominal 1,000,000 tpa carbon-in-pulp (CIP) plant at a pulp density of 50% solids. Stoichiometric reactions of the relevant reagents for each of the four processes were assumed with reaction extents of 95% with cyanide and 15% with thiocyanate (90% for Caro's acid). Reagent costs were based on an average of values listed online [11], adjusted for an assumed annual 3% CPI.

Scenarios tested included oxide ore (0 mg/L SCN) and sulphide ore (300 mg/L SCN), each at a range of cyanide levels. Metals were ignored in the calculations, as were copper sulphate additions.

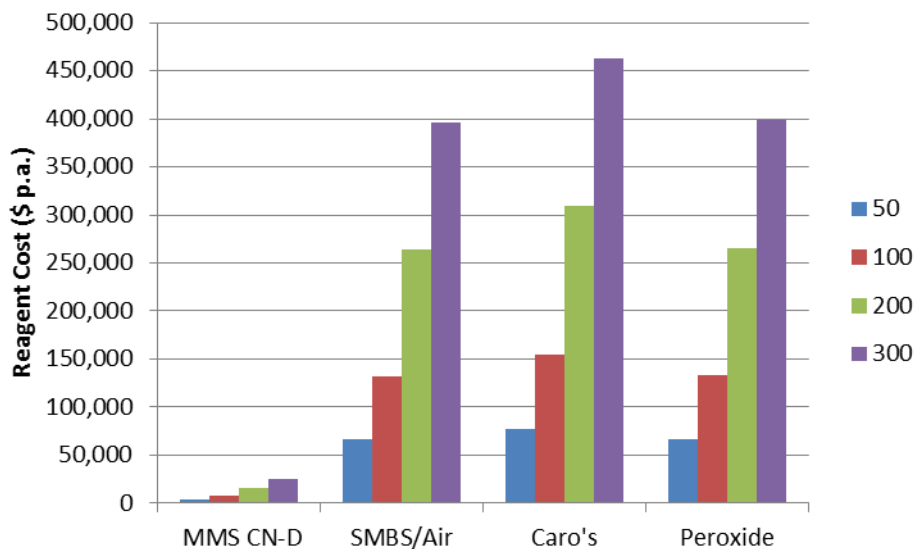
Cost Model Outputs

The model outputs are summarized in Figure 2, showing a comparison of reagent costs for cyanide destruction processes at cyanide levels of 50, 100, 200 and 300 mg/L. Costs for the Caro's acid route are higher than the other routes, and this effect is substantially magnified in the case of the sulphide ore (300 mg/L SCN) as compared with the oxide ore (0 mg/L SCN). SMBS/Air and hydrogen peroxide routes report somewhat reduced reagent costs, while MMS CN-D™ reagent costs are significantly lower than those of the other three cyanide destruction process routes considered.

Several factors need to be considered that may impact on reagent consumptions in practical applications of these processes:

- Additional side reactions, e.g. peroxide hydrolysis and decomposition, were not considered.
- Reagent dissolution and formation efficiencies were not considered – Caro's acid is typically produced *in situ* at the plant at comparatively low efficiencies.
- The effect of solids on the reactions was not considered – solid mineral phases may attenuate free and complexed cyanides by adsorption and precipitation; moreover, reagents such as hydrogen peroxide are known to react substantially with pulp solids.
- Many CIP plants have oxygen available onsite at excess capacity to enhance leach kinetics, potentially eliminating transportation costs for this reagent.

(a)



(b)

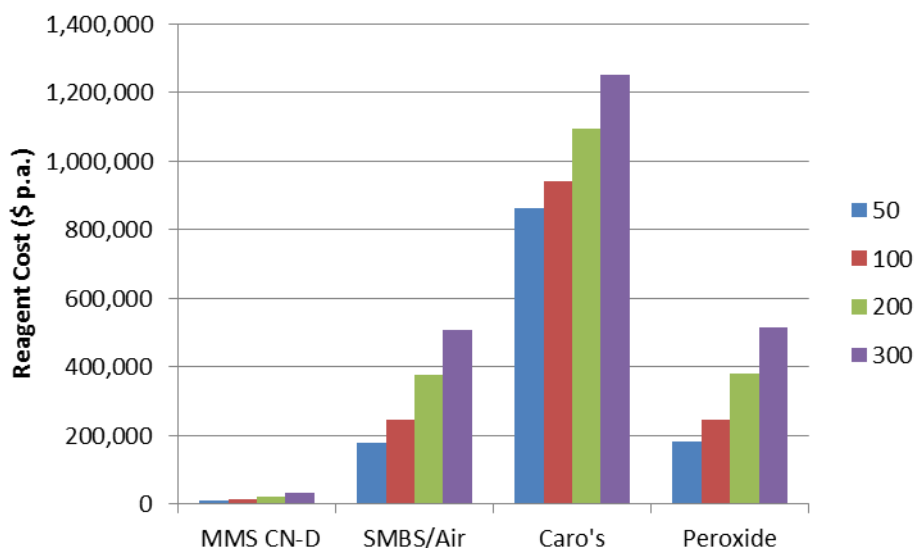


Figure 2: Reagent cost comparison for cyanide destruction processes at cyanide levels of 50, 100, 200 and 300 mg/L – (a) oxide ore (0 mg/L SCN) and (b) sulphide ore (300 mg/L SCN)

MMS CN-D™ CYANIDE DESTRUCTION PROCESS – RECENT TESTWORK

Significant bench and pilot-scale testwork has been completed at Maelgwyn Mineral Services Africa, where the concept was originally developed [2]; the first full-scale MMS CN-D™ plant has been constructed at a gold plant in East Africa and is currently awaiting CIP plant stabilization and commissioning. Recent testwork has been carried out at Maelgwyn Australia on samples from several gold operations; moreover, the process has been further developed and demonstrated on gold tailings effluent at pilot and continuous bench-scale [12]. An example of pilot scale results is shown in Figure 3 for illustrative purposes, indicating significant reductions in both cyanide and thiocyanate in this particular test.

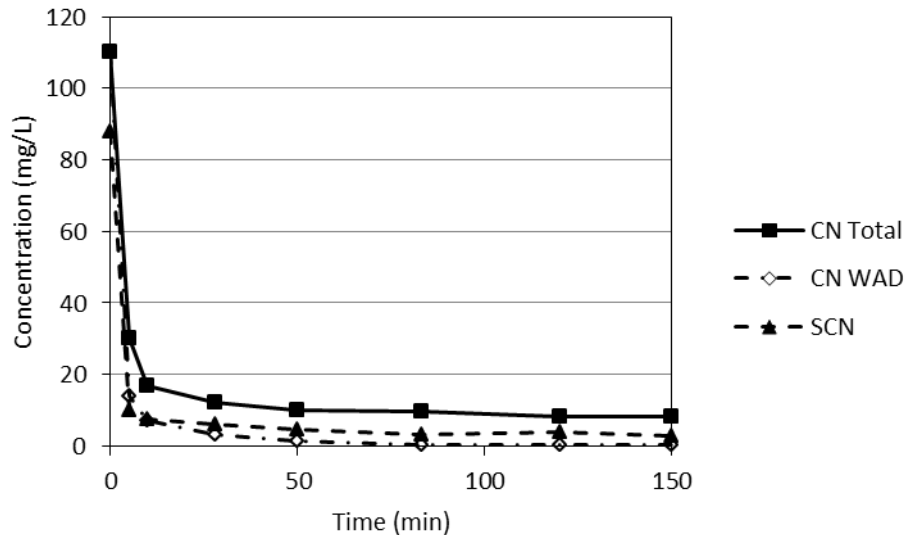


Figure 3: Pilot-scale MMS CN-D™ cyanide destruction test data (after Adams and Glen [12])

CONCLUSIONS

The MMS CN-D™ Process is shown to have considerable potential qualitative upside in comparison to the three most common oxidative cyanide destruction process routes. Oxidative reagent transportation, storage, mixing, dosing and safe handling are clear potential issues for the SMBS/Air, Caro's acid and peroxide processes. Environmental issues such as elevated salt and sulphate loads due to sulphur addition, as well as the risk of corrosive contamination of wildlife habitats on overdosing excursions, are additional factors to be considered when implementing conventional chemical dosing cyanide destruction methods. These factors become particularly important in both remote sites and sites located close to urban areas.

From the reagent cost model outputs for a nominally typical gold plant requiring a comparison of the four options considered in this paper, the following can be concluded:

- Costs for the Caro's acid route are higher than the other routes.
- This effect is substantially magnified in the case of the sulphide ore (300 mg/L SCN) as compared with the oxide ore (0 mg/L SCN).
- SMBS/Air and hydrogen peroxide routes report somewhat reduced reagent costs.
- MMS CN-D™ reagent costs are significantly lower than those of the other three cyanide destruction process routes considered.

Additional upside potential exists in the case of the MMS CN-D™ Process, given that additional gold leaching is expected in some cases, due to mineral surface cleaning in the high-shear cavitation zone of the Aachen Reactor™, along with enhanced gold adsorption equilibrium onto the CN-D™ carbon, subject to carbon movement. Significant bench and pilot-scale testwork has been completed. The first full-scale MMS CN-D™ plant has been constructed at a gold plant in East Africa and is currently awaiting CIP plant stabilization and commissioning.

REFERENCES

1. T. Gibbons, "International Cyanide Management Code", *Advances in Gold Ore Processing*, M.D. Adams, Ed., Elsevier, Amsterdam, 2005, 182-200.
2. A. Singh, "Removal of Cyanide from Aqueous Streams", Worldwide Pat. No. PCT/IB2008/054806, 17th August 2008.
3. M.D. Adams, "The Chemistry of Cyanide in the Extraction of Gold. 1. Kinetics of Cyanide Loss in the Presence and Absence of Activated Carbon", *J. S. Afr. Inst. Min. Metall.*, Vol. 90, No. 2, 1990, 37-44.
4. M.D. Adams, "The Chemistry of Cyanide in the Extraction of Gold. 2. Mechanisms of Cyanide Loss in the Carbon-in-Pulp Process", *J. S. Afr. Inst. Min. Metall.*, Vol. 90, No. 3, 1990, 67-73.
5. M.D. Adams, "Removal of Cyanide from Solution using Activated Carbon", *Minerals Engineering*, Vol. 7, No. 9, 1994, 1165-1177.
6. M.M. Botz, T.I. Mudder and A.U. Aksil, "Cyanide Treatment: Physical, Chemical and Biological Processes", *Advances in Gold Ore Processing*, M.D. Adams, Ed., Elsevier, Amsterdam, 2005, 672-702.
7. E.A. Devuyt, B.R., Conard, R. Vergunst and B. Tandi, "Cyanide Removal Process Using Sulfur Dioxide and Air", *J. Metals*, Vol. 41, No. 12, 1989, 43-45.
8. O.B. Mathre, and F.W. DeVries, "Destruction of Cyanide in Gold and Silver Mine Process Water", *Gold and Silver Leaching, Recovery and Economics*, W.J. Sblitt, W.C. Larson and J.B. Hiskey, Eds., American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., Littleton, Colorado, 1981, 77-82.
9. A. Griffiths, M.Q. Ahsan, R. Norcross, H. Knorre and F.W. Merz, "Process for Generating an Oxidizing Reagent for the Treatment of Polluted Water", U.S. Patent No. 4,915,849, 10 April 1990.
10. S. Flatman, M. Battersby, R. Imhof, R.M. Battersby and S. Ibrayev, "The Leachox Refractory Gold Process - The Testing, Design, Installation and Commissioning of a large Scale Plant at the VASGOLD Gold Mine, Kazakhstan", *Precious Metals '10*, Falmouth, Cornwall, UK, June 2010. 24 pp.
11. Online chemical cost databases and other sources (<http://www.icis.com/StaticPages/a-e.htm>; <http://www.buzzle.com/articles/how-to-make-liquid-oxygen.html>; accessed 29th April 2011).
12. M. Adams and S. Glen, "Pilot-Scale and Continuous Bench testing of the MMS CN-D™ Cyanide Destruction Process on an Australian Gold Plant Tailings Effluent", *World Gold 2011*, CIM, Montreal, 2011, submitted for publication.