PILOT-SCALE AND CONTINUOUS BENCH TESTING OF THE MMS CN-D™ CYANIDE DESTRUCTION PROCESS ON AN AUSTRALIAN GOLD PLANT TAILINGS EFFLUENT

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ABSTRACT

Cyanide management practices on modern gold plants are becoming more onerous, due to environmental pressures, particularly for signatories to the International Cyanide Management Code. Operations are therefore seeking to reduce levels of weak-acid dissociable (WAD) cyanide reporting to spigot discharge as well as to any eventual discharges from the tailings storage facility (TSF).

Current gold industry standard processes primarily include the oxidation of cyanide by means of sodium meta-bisulfite (SMBS, or SO₂) with air, Caro’s acid (H₂SO₅) or hydrogen peroxide (H₂O₂). These processes require the transport and usage of expensive oxidizing reagents, along with the safety and environmental issues associated with these corrosive and toxic chemicals. 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 and no additional reagents, to increase the rate of cyanide oxidation to cyanate, the thermodynamically more stable form.

Testwork conducted at the Maelgwyn Australia testwork facility in Perth Australia is described, at both pilot scale and continuous bench-scale, on a sample of tailings effluent obtained from an Australian gold plant. WAD cyanide is demonstrated to be lowered using the MMS CN-D™ process from an influent of 130 mg/L to the required levels for discharge to TSF (<50 mg/L). The continuous test results showed stable operation over three residence time turnovers. The pilot-scale results demonstrated the efficiency of the process at the reasonably large scales required for engineering cost estimation.

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INTRODUCTION

Management of cyanide in gold plant tailings effluents and discharge streams is an important consideration in the design and operation of modern gold process plants. Environmental stewardship is a driver, with many companies signed up to the International Cyanide Code. For technical reasons also, in particular plants treating refractory gold ores require dam return water to be low in cyanide to avoid unplanned depression of sulphide mineral flotation or bacterial kill in bioleaching processes – this is common practice and examples may be found in the public domain on Government Environmental Department websites, publishing various gold mining operations' Environmental Assessment Reports for their Environmental Licences.

Signatories to the International Cyanide Management Code require their operations to reduce levels of weak-acid dissociable cyanide (WADCN) reporting to spigot discharge, typically to <50 mg/L, as discussed by Gibbons [1]. In cases where discharge of effluent solution to the environment is necessary, levels of total cyanide (TCN) below 0.5 mg/L may be required; however, control of spigot discharge to TSF is by far the main application of cyanide destruction in the gold industry.

The main routes for cyanide removal from gold plant tailings and effluents include the oxidation of cyanide by means of sodium meta-bisulfite (SMBS, or SO$_2$) with air, Caro’s acid (H$_2$SO$_5$) or hydrogen peroxide (H$_2$O$_2$). 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, ultimately decomposing to carbon dioxide and nitrogen. The current work was aimed at testing the CN-D™ process at both pilot scale and continuous bench-scale, on a sample of tailings effluent obtained from an Australian gold plant.

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$_2$O$_2$) process, and the Caro’s acid (H$_2$SO$_5$) 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 (Na$_2$S$_2$O$_5$) or sodium sulfite (Na$_2$SO$_3$), along with copper (II) sulfate as catalyst if insufficient copper is present in solution. The reaction depicted in Equation (1) applies:

$$\text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} + \text{CN}^- \rightarrow \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^*$$  \hspace{1cm} (1)
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$_2$O$_2$, along with copper (II) sulfate as catalyst if insufficient copper is present in solution. The relevant chemical reaction is depicted in Equation (2):

$$\text{H}_2\text{O}_2 + \text{CN}^- \rightarrow \text{OCN}^- + \text{H}_2\text{O}$$  \hspace{1cm} (2)

The theoretical usage of H$_2$O$_2$ in the process is 1.31 g of H$_2$O$_2$ per gram of CN$^-$ oxidized, but in practice, usage of 2.0-8.0 g H$_2$O$_2$ 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$_2$SO$_5$, known as Caro’s acid). The formation and cyanide oxidation chemical reactions are depicted in Equations (3) and (4), respectively:

$$\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{SO}_5 + \text{H}_2\text{O}$$  \hspace{1cm} (3)

$$\text{H}_2\text{SO}_5 + \text{CN}^- \rightarrow \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+$$  \hspace{1cm} (4)

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$_2$SO$_5$ in the process is 4.39 g of H$_2$SO$_5$ per gram of CN$^-$ oxidized, but in practice, usage of 5.0-15.0 g H$_2$SO$_5$ 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$^{\text{TM}}$ Cyanide Destruction Process**

The MMS CN-D$^{\text{TM}}$ Cyanide Destruction Process [2] utilizes the Aachen Reactor$^{\text{TM}}$. This concept for mineral slurry reactors originated in Germany, and was originally developed in the 1970s for applications in flotation. The Aachen Reactor$^{\text{TM}}$ 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$^{\text{TM}}$-assisted leaching of gold ores with cyanide and high-rate oxidation of sulphides (Leachox$^{\text{TM}}$ 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$^{\text{TM}}$ 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 [5-8]:

\[
\begin{align*}
2\text{OH}^- + \text{CN}^- & \rightarrow \text{OCN}^- + \text{H}_2\text{O} + 2e^- \quad (E = -0.97 \text{ V}) \\
\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- \quad (E = 0.40 \text{ V}) \\
\text{CN}^- + \frac{1}{2}\text{O}_2 & \rightarrow \text{OCN}^- \\
\text{OCN}^- + 2\text{H}_2\text{O} + \text{H}^+ & \rightarrow \text{NH}_4^+ + \text{HCO}_3^-
\end{align*}
\]

LabLox™ CN-D™ Reactor

The LabLox™ CN-D™ Reactor is a bench-scale MMS CN-D™ Cyanide Destruction Process simulation that combines the two stages of super-oxygenation and carbon-contact in a single bench-scale reactor. This unit is designed for laboratory simulation testing only with the aim to rapidly amenability test potential CN-D™ and Leachox™ applications and lacks the oxygen and reagent utilization and energy efficiencies inherent in using actual Aachen Reactors™.

Super-oxygenation is achieved by feeding pure oxygen directly into a high-speed, high-shear impellor whilst carbon-contact simultaneously occurs at the periphery of the reaction vessel. Slurry mixing and particle suspension is promoted by the turbulent action of the impellor and carbon attrition is minimised by the segregation of the carbon away from the high-shear impellor by a carbon-exclusion cage.
For continuous testing, a bulk sample is fed into the LabLox™ CN-D™ Reactor via a dosing pump. The sample is fed directly into the high-shear impellor in order to prevent short-circuiting of the fresh liquor to the outlet and a constant volume is maintained within the reactor vessel by liquor overflow. The overflow falls to a carbon screen after which the CN-D™ detox liquor flow rate is monitored, the liquor collected for sampling and the overflow carbon returned to the reactor vessel.

Figure 2 – LabLox™ CN-D™ Reactor for bench-scale Aachen Reactor™ simulation of the MMS CN-D™ Process

**EXPERIMENTAL PROCEDURE**

**Test Sample and Reagents**

A 1,000 L tailings slurry sample from an Australian gold plant was provided in a well-sealed bulky container. The solids were allowed to settle overnight and two samples of the solution were collected from the middle of the supernatant for testing. The solution samples were held in well-sealed buckets and protected from light and heat prior to testwork. Head samples were taken from the stirred solutions for head assays.

Pure oxygen was provided by BOC Gas in cylinder form. All other reagents used were AR grade supplied by Rowe Scientific. Perth tap water was used throughout the testwork programme.

Virgin activated carbon was supplied in sealed 20 L buckets by the gold plant. The carbon was pre-abraded by water slurrying and rolling overnight before screening at 1 mm and displacement water-washing to remove fines and solubles.
Continuous Bench-Scale Testwork

A 22 L sample of tailings solution was decanted into a covered container and a 5.5 L charge pumped into the LabLox™ CN-D™ Reactor vessel. A 50 g/L activated carbon charge was added to the reactor vessel and oxygen was introduced. The initial charge was left to condition to an approximate equilibrium for two hours at a pH value of ~9, with interim samples taken periodically, before the overflow valve was opened and the excess charge allowed to drain, leaving 4.5 L of conditioned liquor. A continuous flow of fresh cyanide tailings liquor was then pumped into the reactor vessel to give a residence time of two hours for an additional six-hour period and allowing a full three turnovers of reactor contents. Samples were taken periodically and SCN, WAD and Total CN samples submitted for analysis at MPL Laboratories (colorimetrically by a NATA accredited procedure) whilst Free CN was determined by Maelgwyn Australia (titration with AgNO₃ and rhodanine indicator).

Pilot-Scale Testwork

A 65 L charge of tailings solution was decanted into a 70 L sealed stainless steel column. The solution was then pumped through an oxygen-fed Aachen Reactor™ under common sealed system and recirculated back into the column for a nominal 30 minute pre-oxygenation conditioning phase. The solution was then pumped through an oxygen-fed Aachen Reactor™ and recirculated back into an open tank containing 50 g/L activated carbon for a 120 minute CN-D™ cyanide destruction phase. Samples were taken periodically and submitted for analysis at ChemCentre of Western Australia using standard ASTM procedures (cyanides by segmented-flow autoanalysis and metals by ICP-OES/MS).

Instrumentation and Control

Both the bench-scale and pilot-scale rigs incorporated separate Siemens control systems for data logging of pH, temperature, dissolved oxygen (DO) and oxidation-reduction potential (ORP, or Eh). The pilot-plant control system also logged system pressures at various points. These systems enabled rapid real-time adjustment of conditions to ensure smooth adherence to control setpoints.

RESULTS AND DISCUSSION

Head Analysis

The tailings solution at the commencement of the MMS CN-D™ testing analysed some 130 mg/L WAD and total cyanide and 58 mg/L free cyanide. Metals were generally low (<5 mg/L), and including a small amount of copper. Detailed mechanistic analysis of the behaviour of the various metals in the system was beyond the scope of the present study and shall be examined in future work.
Table 1 – Tailings solution head analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN Free</td>
<td>58</td>
</tr>
<tr>
<td>CN WAD</td>
<td>130</td>
</tr>
<tr>
<td>CN Total</td>
<td>150</td>
</tr>
<tr>
<td>SCN</td>
<td>88</td>
</tr>
<tr>
<td>OCN</td>
<td>8</td>
</tr>
</tbody>
</table>

Continuous Bench-Scale Testwork

Free and WAD cyanide were both reduced by 90% in the 120 min conditioning period, whilst total cyanide and SCN were reduced by 73% and 43%, respectively, as shown in Figure 3. After the conditioning period, concentrations of WAD and total cyanides shifted to a dynamic equilibration point that appeared to be achieved after about 400 min. Thiocyanate levels equilibrated close to their initial concentration at the termination of the test – thiocyanate levels not required to be lowered for Cyanide Code compliance. Free cyanide levels remained at low levels (~5 mg/L) throughout, as expected for efficient cyanide oxidation in this system. In the application under consideration, spigot discharge to tailings storage facility is simulated and the results show WAD cyanide <50 mg/L at equilibration, consistent with Cyanide Code compliance.

![Figure 3 – LabLox™ CN-D™ Reactor eight-hour continuous cyanide destruction test data](image)

Solid mineral phases are well known to attenuate cyanide by adsorption and precipitation, particularly at low free cyanide levels. Preliminary results obtained on MMS CN-D™ testing of various cyanide tailings pulps are consistent with a further enhancement of cyanide destruction efficiency over and above solution...
phase results. This result is consistent with previous work on the cyanide-carbon system and the possibility of co-catalysis of cyanide oxidation by carbon and copper [5, 11].

Continuous pilot-scale testing of the MMS CN-D™ Process over suitably extended periods appears warranted to enable the determination of more detailed design criteria and operation parameters.

Pilot-Scale Testwork

WAD and free cyanide as well as thiocyanate were removed to <10 mg/L levels in less than 10 minutes of reaction time, as illustrated in Figure 4. Under these conditions, lower total cyanide (~10 mg/L) levels were achieved, suggesting that operating parameters may be modified to suit various targeted WAD and total cyanide levels in final discharge, e.g. to TSF, process plant or as final effluent. Cyanate (OCN⁻) was 8 mg/L at the start and 12 mg/L at the end of the test.

![Figure 4](image)  
Figure 4 – Pilot-scale MMS CN-D™ cyanide destruction test data

CONCLUSIONS

The MMS-CN-D™ Process has been demonstrated on a gold plant slurry at both continuous bench-scale and semi-continuous pilot-scale. The continuous test results showed stable operation over three residence time turnovers. The pilot-scale results demonstrate the efficiency of the process at reasonably large scales, yielding data suitable for first-pass cost estimation of commercial-scale MMS CN-D™ plants. Continuous testing on a gold plant tailings solution showed WAD cyanide levels reduced from an influent of 130 mg/L to a terminal effluent of <50 mg/L. In the application tested, no additional reagents were added, oxidation was achieved by use of oxygen only, catalysed via super-oxygenation in the Aachen Reactor™ with carbon. Oxygen is typically readily available onsite for enhancement of leach kinetics and indeed, several commercial applications exist where Aachen Reactors™ are used for this duty. The comparative cost safety and
environmental issues of this route against transportation and usage of oxidizing chemicals for cyanide destruction is considered to be inherently favourable and warrants serious evaluation on a case by case basis.

While the current example utilized solutions, the system is designed to allow for testing of slurries and both the bench-scale and pilot-scale rigs have been demonstrated on other applications using slurries. Subsequent continuous pilot-scale testing of the MMS CN-D™ Process using multi-stage rigs is under current design consideration for application at various larger scales onsite at operating gold plants over suitably extended periods. This will enable the determination of more detailed design criteria and operation parameters on a site-specific basis. The first MMS CN-D™ commercial plant is currently installed at a gold plant in West Africa and is awaiting upstream plant stabilization prior to unit conditioning.

Additional features of the MMS CN-D™ process may also be considered, such as the potential to recover additional gold otherwise lost to tailings, the potential to de-risk implementation and lower capital costs via staged integration of Aachen Reactors™ into existing oxygenation and SO₂/Air equipment and the potential to modify existing plant tankage in underutilized or overdesigned CIL trains to become part of the MMS CN-D™ cyanide destruction plant component. Potential capital and operating costs for such a plant typically showing considerable upside benefit compared with those obtained for the alternative cyanide destruction processes.

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REFERENCES


