



Bespoke field columns to assess hexavalent chromium risk for refinement of mine closure plans

Julia Dent¹, Martin Williams², Bakary Draba³

¹Senior consultant, WSP UK Ltd., 2 Queen St., Manchester, M2 5JB, UK, Julia.dent@wsp.com

²VP for Europe/Africa / Group Chief Geochemist, Piteau Associates, 25 Rudd Rd, Illovo, Johannesburg, Gauteng, South Africa, 2196

³Plant Manager, AngloGold Ashanti, Yatela Mine, Mali

Abstract

Yatela mine in Mali operated a heap leach pad (HLP) to recover gold for 20 years until 2017. Ore placed on the HLP was routinely agglomerated using cement. In early operations cement contained around 200 mg/kg of chromium, predominantly as Cr⁶⁺. On termination of irrigation in 2017, a solution inventory of >100,000 m³ prevailed containing Cr⁶⁺ at a concentration of >4 mg/L. The Yatela Closure Plan (YCP) contemplates rinsing of the HLP to remove residual contaminants from the pore solution. However, the risk of long-term mobilization Cr⁶⁺ from the spent ore is uncertain. An experimental assessment was initiated in 2017 involving six test columns each filled with sub-samples of 80 kg of ore from the HLP. Different solutions were applied to each column with variability in pH, plus in some instances variable levels of Ba(OH)₂ as a prospective reagent to induce Cr immobilization. While high concentrations of Cr⁶⁺ (>1.5 mg/L) were observed in initial column leachate, concentrations declined to <0.01 mg/L within a month of the onset of irrigation. The Cr⁶⁺ concentration reduction appears partially correlated to pH. Column irrigation at ambient rainfall pH resulted in rapid reduction of Cr⁶⁺. Columns irrigated with Ba(OH)₂ solution showed Cr⁶⁺ attenuation trends analogous to those irrigated by near-neutral water. The efficacy of Ba(OH)₂ for Cr immobilization appears restricted by difficulties sustaining the compound in solution, competition from SO₄ and increased column ambient pH.

Keywords: Mine closure, Heap leach pads, Hexavalent chromium, Field columns

Introduction

Yatela is an open pit gold mine, located in western Mali approximately 50 km south-west of the regional centre of Kayes. Mining was initiated in 2001 and terminated in 2013, although processing of gold continued to 2017. Throughout operations, gold recovery was undertaken through the crushing, agglomeration and heap leaching of ore using NaCN solution. Pregnant leach solution (PLS) reporting to the base of the heap leach pad (HLP) was stripped using activated carbon. Gold was then recovered in a refinery to produce doré. The HLP consists of a series of cells approximately 850 m long by 80 m wide and up to 24 m high. There are 20 full size cells, some of which are sub-divided. The HLP occupies an area of approximately 175 ha and holds a total rock mass of 36 million tons.

As Yatela entered its closure phase in 2017, a particular complexity was recognized to relate to the potential risk of long-term release of hexavalent Cr from the pad. During the early period of operations, the cement used to agglomerate ore was sourced from a location in Senegal in which the firing kilns for cement production were lined with ferrochrome steel. This resulted in mobilization of Cr⁶⁺ into the cement during production. Within the HLP, re-mobilization of Cr⁶⁺ has occurred with attendant generation of high levels of Cr⁶⁺ (typically around 4 mg/L) in the PLS.

A rinsing plan for the HLP currently forms part of the approved Closure Plan for Yatela, principally with the objective of eliminating residual CN compounds from the pore water inventory. Any continued mobilization of Cr⁶⁺ from the ore mass during rins-



ing would, however, significantly undermine the value of rinsing as continued generation of contaminated solution would occur. The Closure Plan currently envisages addition of $\text{Ba}(\text{OH})_2$ to the rinse solution as a mechanism for immobilizing Cr as a low-solubility barium chromate compound. This, however, carries a substantial cost and is of unproven efficacy.

Historical monitoring data for the heap leach circuit suggest that elevated Cr^{6+} levels now prevail largely in solution emanating from the more recently stacked and irrigated cells of the HLP. This supports the assertion that either Cr^{6+} has been flushed from the system, or a control on Cr^{6+} mobilization, such as pH, is influential in the older pads. To assess this assertion, and in conjunction to determine the value of supplementation of rinse solution with $\text{Ba}(\text{OH})_2$, a series of controlled column tests were initiated at Yatela in 2017, as described in this paper.

Methodology

The Yatela column test program was designed with the central objective of establishing an understanding of the mobilisation controls and exhaustion rates of hexavalent Cr in the spent ore on the HLP. The columns were also designed to determine the extent to which $\text{Ba}(\text{OH})_2$ may enhance Cr^{6+} immobilisation within the ore matrix, and any risks of Cr^{6+} remobilisation following the cessation of $\text{Ba}(\text{OH})_2$ addition.

Six columns were set-up in the Yatela Metallurgical Laboratory in March 2017. The columns were 300 mm diameter by 1 metre in height and were each filled with 82 kg of spent ore, recovered from Cell 19A on the HLP. The columns were set-up as follows:

- The columns were made from high grade plastic (PTFE) which may be considered extremely unlikely to leach inorganic constituents.
- Spent ore was uniformly crushed to <3 cm.
- The columns were housed under cover (in the metallurgical testing laboratory) to avoid any infiltration of rainfall.
- The columns contained a drainage vent and tubing at the base, through which solution was routed to a collection canister.
- Collection vessels of 10 litres in volume were placed at the base of each column.
- Dripper systems were emplaced to administer solution at a rate of 3 ml/minute to each column. This was confirmed experimentally to allow free solution flow without saturation.

The methodology for column operation is outlined in Table 1. Key points include:

- a) All columns were irrigated with identical raw water for the first 72 hours. This was sourced from the Raw Water Pond at Yatela and had a slightly alkaline pH. This common irrigation procedure for the first 72 hours was intended to allow confirmation of the comparability of Cr concentrations emanating from each column.
- b) With effect from day 4, each column was irrigated with a unique solution as shown in Table 2. Column YT-2 was acidified to ensure a solution pH (entering) of 5.5. For each column, solution conditions remained unchanged until day 30.
- c) A critical aspect of YT-05 was the use of monitoring pond water.
- d) From days 31 to 50 the columns were allowed to drain. Solution was collected for analysis at approximately weekly intervals, if present.
- e) From days 51 to 60 raw water was applied. Column YT02 used water acidified to pH 5.5. The aim of this phase of the column tests was to simulate leaching by rainfall following a period of rinsing, plus drain-down.

Two sample suites were collected to analyse column leachates. The first was used specifically to measure pH, temperature, electrical conductivity (EC), dissolved oxygen and hexavalent chromium (by colorimetry) on site at Yatela. The second was shipped to a laboratory in the UK (Exova Jones) for analysis of hexavalent chromium, major cations, major anions, trace metals and cyanide species. Leachate was sampled daily during Step 1 and weekly during Steps 2 and 3 as defined in Table 1.



Table 1 Bespoke column test methodology steps

Column	Test duration (days)	Step 1	Step 2		Step 3	Step 4	
		Days 1 to 3	Days 4 to 30	Reagent addition	Days 31 - 50	Days 51 to 66	Reagent addition
YT01	66	Raw water or tap water (pH <7.8)	Raw water or tap water (pH <7.8)	None	No irrigation	Raw water or tap water (pH <7.8)	None
YT02	66	Raw water or tap water (pH <7.8)	Water (pH 5.5)	HCl (few drops)		Water (pH 5.5)	HCl (few drops)
YT03	66	Raw water or tap water (pH <7.8)	Raw Water or tap water + Ba(OH) ₂	50 mg/L Ba(OH) ₂ in solution		Raw water or tap water (pH <7.8)	None
YT04	66	Raw water or tap water (pH <7.8)	Raw Water or tap water + Ba(OH) ₂	5 mg/L Ba(OH) ₂ in solution		Raw water or tap water (pH <7.8)	None
YT05	66	Raw water or tap water (pH <7.8)	Monitoring pond + Ba(OH) ₂	50 mg/L Ba(OH) ₂ in solution		Raw water or tap water (pH <7.8)	None
YT06	66		Raw water or tap water + Fe ₂ SO ₄	50 mg/L Fe ₂ SO ₄ in solution		Raw water or tap water (pH <7.8)	None

Table 2 Initial analysed chromium and hexavalent chromium abundances in column test material

Sample	Hexavalent Chromium (CrVI)	Total Cr	Cr2O3
	mg/kg	mg/kg	%
YAT01	1.75	58	0.02
YAT02	1.61	72	0.02
YAT03	1.70	71	0.02
YAT04	1.79	67	0.02
YAT05	0.44	76	0.02
YAT06	1.01	75	0.02

Results

The results Cr and Cr⁶⁺ head-grade assays for each column are shown in Table 2. Daily hexavalent chromium analyses of column leachates are presented in Figure 1. These show that Cr⁶⁺ concentrations in all columns declined from initial levels of >2 mg/L to near zero by around day 10 of initiation, with no significant differentiation evident between columns with and without barium hydroxide

addition. The Cr concentration decay curve occurred in response to a pore-volume transfer rate of approximately 0.5 per week, thus equating to slightly less than one full pore volume in total. The persistence of concentrations of Cr⁶⁺ in the very low part per billion range was then observed throughout the remaining testing period in columns YAT01 and YAT02, which were irrigated with raw water at pH levels of 7.8 and 5.5 respectively.



In contrast, measured hexavalent chromium levels appeared to increase with effect from day 12 in all solutions subject to $\text{Ba}(\text{OH})_2$ addition.

The addition of $\text{Ba}(\text{OH})_2$ was observed to produce an alkaline irrigation solution. This appears to increase Cr^{6+} stability in solution and overwhelms any potential benefit which could otherwise arise with respect to Cr immobilization through barium chromate precipitation. Further, concentrations of SO_4 in the leachates of columns subject to $\text{Ba}(\text{OH})_2$ addition were reported to decline in a sequence inversely correlated to the molarity of reagent addition. This suggests that Ba is preferentially consumed in barite precipitation, with little reactive Ba available for Cr immobilization. This, in conjunction with the persistently low Cr^{6+} concentrations observed in columns YAT01 and YAT02 to which raw water of neutral to weakly acidic pH with no additional reagent was applied, confirms that barium hydroxide addition is unlikely to be warranted in any future field-scale rinsing of the Yatela HLP. This prospectively reduces the cost of Yatela’s current Closure Plan strategy for the HLP by more than US\$ 1 million.

A key aspect of the column test design was inclusion of a cessation of irrigation at Step 2, a subsequent drain-down period of 20 days (Step 3) and finally the re-initiation of irrigation for a 10 day period using clean water (Step 4). These steps were considered critical for understanding the risk of remobilization of Cr^{6+} following field-scale HLP rinsing by residual long-term rainfall infiltration. In the test columns, recommencement of irrigation in Step 4 produced no apparent Cr remobilization in YAT01 and YAT02, with leachate concentrations remaining close to detection limits.

Simple mass balance calculations for each of the six test columns indicate that the reduction trend of Cr^{6+} is in no way related to exhaustion of the available hexavalent Cr inventory in the ore. Instead, the results of all column tests viewed in conjunction suggest that a primary control is ambient pH. Under strongly alkaline conditions, as occurred in the HLP cells during active irrigation with CN, Cr^{6+} is readily stabilized in solution. With falling pH towards a neutral or acid state, this stability is suppressed.

The WAD-CN concentration in column

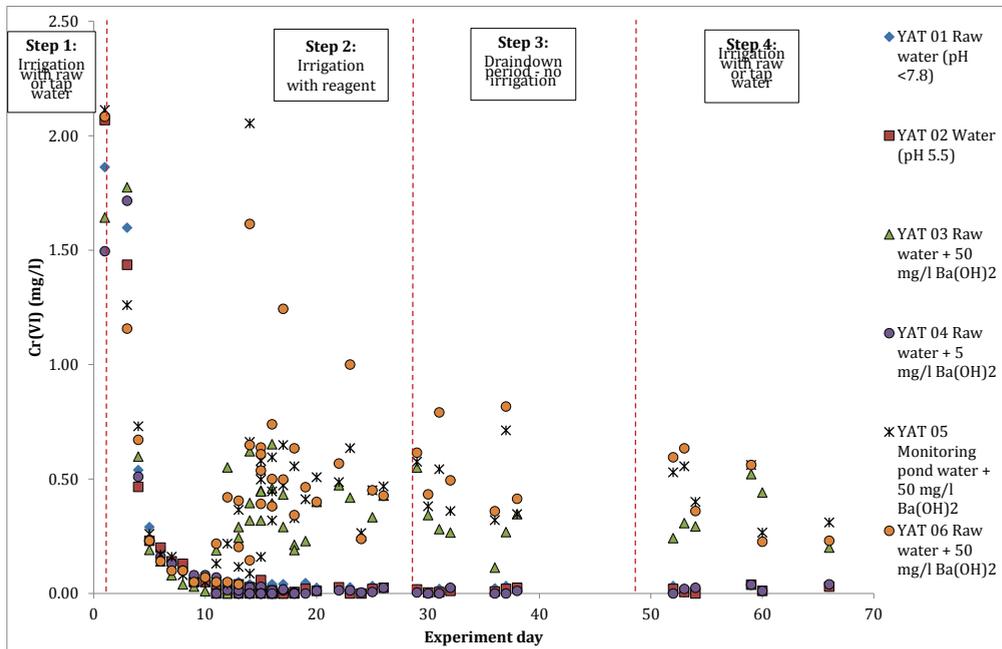


Figure 1 Daily onsite $\text{Cr}(\text{VI})$ analyses of column leachates.



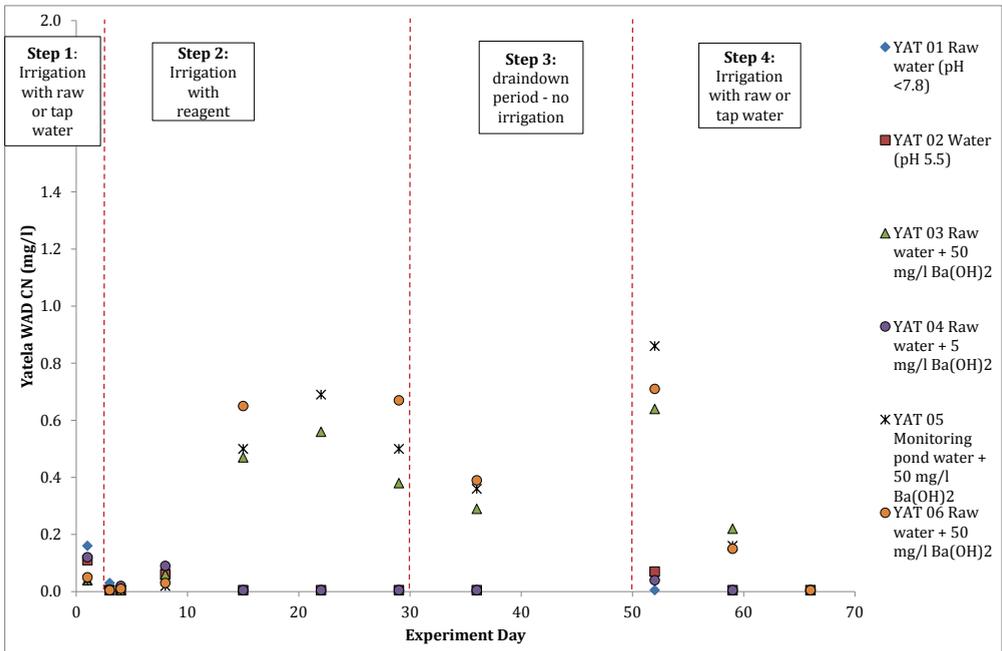


Figure 2 Weekly WAD cyanide analyses of column leachates

leachates was not recorded at levels in excess of 2 mg/L in any column. This is positive as Yatela's completion criterion for rinsing of the HLP is the attainment of a sub- 2mg/L CN threshold. The majority of samples were also below the IFC effluent guideline of 0.5 mg/L WAD-CN. Within a week of test commencement, WAD-CN concentrations in leachates from the columns were typically 0.2 mg/L or less. There appears to be mobilisation of WAD-CN from day 15 of the experiment in the leachate samples YAT03, YAT05 and YAT 06, based on the Yatela and external laboratory data. This coincides with the high concentrations of barium and hexavalent chromium remobilisation in these column leachates. WAD-CN in columns where no barium hydroxide is added (YAT01 and YAT02) remain at a low concentration of WAD-CN, often below detection limits, following the initial flush of WAD-CN in the first week of irrigation and sampling. The apparent mobilisation of WAD-CN in columns where barium hydroxide could be related to the high pH caused by the barium hydroxide. However, as the pH of the other columns is also relatively high (Figure 2) it is more likely to be a direct effect of the addition of barium hydroxide and either

chemical remobilisation due to this, perhaps from redox effects, or measurement interference. As WAD-CN in column leachates with no barium hydroxide addition is successfully lower than Closure Plan and regulatory requirements the column experiments verify the rinsing plan for this parameter.

Conclusions

The column tests performed at Yatela during 2017 to assess potential long-term risks of hexavalent Cr mobilization from the Yatela HLP have provided valuable guidance in the refinement of a defensible Closure Plan for the facility. The results also suggest that considerable cost-savings may be achieved through elimination of previously held concepts regarding the addition of $\text{Ba}(\text{OH})_2$ to irrigation solution during rinsing of the HLP. The experimental scale data suggest that high levels of Cr^{6+} mobilization during active irrigation of the HLP with CN solution were at least in part attributable to the highly alkaline nature of the solution. To some extent, such mobilization may be anticipated to attenuate naturally following rinsing and the establishment of conditions in which infiltrating solution is of a pH approximating rainwater.



The reduction of leachate Cr⁶⁺ levels to no more than a few parts per billion following only around 1 pore volume of rinsing in test columns subject to raw water irrigation, coupled with the prevalence of CN levels in the leachate which fall substantially below Yatela’s HLP closure completion criterion

of 2 mg/L, suggest that a similar volumetric approach to rinsing plan design may reasonably be adopted for the full scale HLP. This is extremely encouraging, as the overall time-frame for execution of the rinsing plan may need to extend over only a few months.

