Intermediate Report
PU-2016-04-1056

Paste backfill reactivity evaluation – WSP OGR Dalradian mine project (Ireland)

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August 2016

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1. Executive Summary

1.1 Mandate

Annie Lavoie and Jean Philippe Grenier from WSP (hereafter called "client") has contacted the *Unité de recherche et de service en technologie minérale* of the *Université du Québec en Abitibi-Témiscamingue* (URSTM-UQAT) to optimize a cemented paste backfill (CPB) recipe for the Dalradian mine project (North of Ireland). The project targets a CPB plant of a capacity of 900 t/d to fill standard height stopes (around 15 m).

In a first part, the test-work consisted of determining the best binder recipe (among two available binders, Portland cement and blast furnace slag) and a dosage which provide the best mechanical performance constrained by an unconfined compressive strength of 700 kPa after 7-10 days of curing time and the best related cost (see PU-1041-A & B). The objective was reached for CPB recipes made of 5 and 7 % of Slag-GU 70-30 (after 12 and < 10 days, respectively – for more information, see 1041-B).

The objective of the present offer is to characterize[1] cemented past backfill (CPB) made of two recipes (i.e., Slag-GU 70-30 at 5 and 7%) after 28 days of curing time and to evaluate their reactivity. More precisely, the work to be done include the characterization of the mixtures and the production of monolithic leaching tests (MLT).

1.2 Experimental program

For each recipe (i.e., Slag-GU 70-30 at 5 and 7%), the proposed experimental program included the following phases:

- Material preparation (e.g., crushing, homogenization) of the two CPB recipes after unconfined compression tests performed at 28 days (PU-2016-02-1041-B);
- Chemical and mineralogical characterizations of each CPB recipes after 28 days of curing time;
- Monolithic leaching tests (MLT) for two CPB molds made of 5 and 7% of Slag-GU 70-30 after 28 days of curing time.

2. Material and Methods

2.1 Materials preparation

The materials (i.e., CPB samples) were crushed and homogenized in the URSTM-UQAT laboratory prior to chemical and mineralogical characterizations. For the MLT, two CPB molds were previously produced and placed in a humid curing room to be cured at 25°C under 85% relative humidity during 28 days (for more information, see PU-2016-02-1041-B).

[1] The characterisation of each mixture was performed on CPB samples obtained after unconfined compression tests (PU-2016-02-1041-B).

2.2 Characterization of the two CPB recipes

After preparation, the two CPB samples (e.g., Slag-GU 70-30 at 5 and 7%) were characterized by determination of:

- Major element oxides (whole rock analysis – XRF);
- Chemical composition (acid digestion and ICP-AES analysis);
- Total sulphur and carbon contents (induction furnace analyzer);
- Sulphate content (digestion with 40% hydrochloric acid and ICP-AES analysis);
- NP of the acid-base accounting (ABA) before and after weathering tests (Sobek et al. (1978) method modified by Lawrence and Wang (1996));
- Mineralogical composition and semi-quantification by X-Ray Diffraction (XRD) before and after MLT;
- Quantitative mineralogy by optical microscopy and scanning electron microscopy (SEM) analysis before and after MLT.

2.3 Paste reactivity

The environmental behaviors of the two CPB recipes (i.e., Slag-GU 70-30 at 5 and 7%) were evaluated using:

- TCLP (Toxicity Characteristic Leaching Procedure) and SPLP (Synthetic Precipitation Leaching Procedure) tests;
- Monolithic leaching tests (MLT).

The TCLP[2] (Toxicity Characteristic Leaching Procedure) was developed by the US Environmental Protection Agency (EPA) to evaluate the mobility of inorganic species in order to assess whether an industrial residue is considered to be a leachable material. The SPLP[2] (Synthetic Precipitation Leaching Procedure) test was developed by the US Environmental Protection Agency (EPA) to determine the concentration of the inorganic species likely to be leached and to evaluate the possibilities of recovery of non-hazardous industrial waste and management of residual materials processed by stabilisation-solidification. The SPLP test implies more acidic solutions than the TCLP; this test simulates the very worst case where backfill is desegregated and submitted to acidic aqueous environments.

TCLP and SPLP tests were performed for the two CPB recipes made of 5 and 7% of Slag-GU 70-30 after 28 days of curing time.

The MLT is based on the European standard EA NEN 7375:2004. This test is intended to evaluate the dissemination of inorganic compounds out of a known geometry of the monolithic materials under aerobic and saturated conditions. The standard provides eight increasing periods of exposure to sampling ($_{1/4}$, 1, $1_{1/4}$, 4, 9, 16, 36 and 64 days). The extraction liquid used in the tests is demineralized water without adjustment of pH and with a ratio of liquid volume

[2] Centre d’expertise en analyse environnementale du Québec (CEAEQ), 2012. http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA100Lixcom11.pdf

compared to the exposed surface. In each sampling, the water influenced by the sample is completely replaced by new contact water.

Two MLT were performed for the CPB molds made of 5 and 7% of Slag-GU 70-30 after 28 days of curing time and sixteen water samples was subjected to chemical analysis (i.e., pH, Eh, alkalinity, acidity, ion chromatography, ICP); concentrations were normalized to the contact surface.

3. Results

3.1 Chemical and mineralogical characterization

The mineralogical and chemical analyses for the two CPB recipes made of 5 and 7% of Slag-GU 70-30 (after 28 days of curing time) are presented below. *Tables 1* and 2 present the chemical analyses, whereas *table 3* shows the mineralogical analyse. In general, these analyses provided relatively close results. Indeed, the two CPB recipes have similar chemical and mineralogical properties.

Table 1: Major element oxides of the CPB mixtures after 28 days of curing time

Oxides	Unit	**5% Slag-GU 70-30 U52359**	**7% Slag-GU 70-30 U52361**
SiO_2	%	59.6	58.6
Al_2O_3	%	9.90	9.84
Fe_2O_3	%	10.6	10.3
MgO	%	1.28	1.37
CaO	%	3.44	4.26
Na_2O	%	0.78	0.74
K_2O	%	2.40	2.34
TiO_2	%	0.48	0.48
P_2O_5	%	0.08	0.07
MnO	%	0.10	0.11
Cr_2O_3	%	0.04	0.04
V_2O_5	%	0.01	<0.01
LOI	%	8.17	8.29
Sum	%	96.9	96.5
Weight	g	17.8	18.2

The two CPB recipes contain Si in the form of quartz (between 54 and 60% - *tables 1 and 3*) and muscovite (between 22 and 26%). Significant contents of Al, Mg, Na and K are presented for both CPB recipes (*table 2*); they are mainly found in muscovite (*table 3*). Although low amounts of carbon are presented (≈ 0.7%), the total sulphur contents are higher (≈ 5.4%). Indeed, significant amounts of sulfides were found in the uncemented backfill (for more information, see PU-2016-02-1041-B). In addition, it is important to note that higher concentrations of Ca (or

CaO – *tables 1 and 2*) were found in the CPB recipe made of 7% of Slag-GU 70-30 due to the higher binder content. The concentrations of Cu, Ni, Pb and Zn found in both CPB recipes are relatively similar and do not appear high enough to affect the environment. This statement will be confirmed from additional environmental tests presented in the next section.

Table 2: Chemical composition of the CPB mixtures after 28 days of curing time

Parameters	Analytical method	Unit	5% Slag-GU 70-30 U52360	7% Slag-GU 70-30 U52362
Al	ICP-AES	mg/kg	46 280	46830
As		mg/kg	455	449
Ba		mg/kg	1 051	1 093
Be		mg/kg	<5	<5
Bi		mg/kg	<5	<5
Ca		mg/kg	21 760	27 520
Cd		mg/kg	<5	<5
Co		mg/kg	<5	<5
Cr		mg/kg	197	196
Cu		mg/kg	1 581	1 516
Fe		mg/kg	67 380	66 610
K		mg/kg	18 400	18 500
Mg		mg/kg	6 000	6 863
Mn		mg/kg	660	678
Mo		mg/kg	<5	<5
Na		mg/kg	5 030	4 980
Ni		mg/kg	<5	<5
Pb		mg/kg	312	317
S_{tot}		mg/kg	51 520	52 140
Sb		mg/kg	<5	<5
Se		mg/kg	202	200
Sn		mg/kg	<5	<5
Ti		mg/kg	1 220	1 215
Zn		mg/kg	153	153
C_{total}	Induction furnace analyzer	%	0.68	0.71
S_{total}		%	5.42	5.38
$S_{sulphate}$	Digestion with 40% HCl + ICP-AES	%	0.27	0.34

Table 3: Mineralogical characteristics of the CPB mixtures after 28 days of curing time

	Mineral	Unit	5% Slag-GU 70-30 U52359	7% Slag-GU 70-30 U52360
Silicates	Quartz	%	54.06	53.62
	Muscovite	%	22.80	25.75
	Chlorite	%	0.43	0.63
	Albite	%	11.06	7.55
Carbonates	Siderite	%	0.76	0.89
	Calcite	%	2.74	2.75
	Magnesian calcite	%	0.99	0.22
	Dolomite	%	3.04	3.88
Sulphides	Pyrite	%	3.73	4.18
	Chalcopyrite	%	0.39	0.53

Note that the mineralogical analyse (*table 3*) did not showed binder phases; these latter will be identified using the optical microscopy (work in progress).

3.2 Acid-base accounting (ABA)

Table 4 shows the ABA results of the CPB mixtures made of 5 and 7% of Slag-GU 70-30. The CPB was classified as uncertain (-20 kg $CaCO_3$/t < PNN < 20 kg $CaCO_3$/t). Note that the addition of binder increased the neutralization potential values (see PU-2016-02-1041-B).

Table 4: Acid base accounting of the two CPB recipes after 28 days of curing time

	S_{total} (%)	$S_{sulphates}$ (%)	$S_{sulphides}$ (%)	PA (kg $CaCO_3$/t)	C_{total} (%)	$PN_{modifié}$ (kg $CaCO_3$/t)	PNN (kg $CaCO_3$/t)	PN/PA
5% Slag-GU 70-30 U 52360	5.42	0.27	5.15	161.0	0.68	> 120	*Work in progress*	
7% Slag-GU 70-30 U 52362	5.38	0.34	5.05	157.7	0.71	> 120		

3.3 Paste reactivity

3.3.1 TCLP and SPLP tests

In order to investigate the potential leachability of metals and metalloids from the two CPB recipes, TCLP (EPA 1311) and SPLP (EPA 1312) tests were performed. Table 5 presents the results of these tests. The results of the TCLP tests (or SPLP tests) performed on the two CPB samples are relatively similar. For both leaching tests, higher concentrations of Ca were found in the leachates of the CPB sample made of 7% of Slag-GU 70-30 due to the higher binder content. However, the concentrations of metal and metalloid elements (e.g., As, Ba, Ca, Co, Cu, Fe, Li, Mg, Mn, Hg, Mi,Pb, K, Si, Na, Ti, U, Zn) in the TCLP leachates were generally higher than those in the SPLP leachates. In addition, leachate concentrations of Ag, Be, Bi, Cd, Cr, Se, Tl and V were around or below the detection limit for both leaching tests. Indeed, the concentrations measured in the TCLP and SPLP leachates are in compliance with the requirements defined by the Quebec *Directive 019* on the mining industry (MDDELCC, 2012). In summary, TCLP and SPLP results confirmed the low potential leachability of metals and metalloids for the two CPB recipes.

Table 5: TCLP and SPLP results for the two CPB recipes after 28 days of curing time

Parameters	Unit	Detection limit	TCLP		SPLP		*Directive 019*[3]	
			5% Slag-GU 70-30 U52359	7% Slag-GU 70-30 U52361	5% Slag-GU 70-30 U52359	7% Slag-GU 70-30 U52361	FE	AII
Al	*mg/l*	0.006	0.009	0.185	3.56	7.39	-	-
Sb	*mg/l*	0.0001	0.0078	0.0047	0.0327	0.0275	-	-
Ag	*mg/l*	0.0005	<0.0005	<0.0005	<0.0005	<0.0005	-	-
As	*mg/l*	0.0005	0.1076	0.0832	0.0288	0.02	0.2	5
Ba	*mg/l*	0.0005	0.5643	0.6178	0.1208	0.1973	-	100
Be	*mg/l*	0.0005	<0.0005	0.0006	<0.0005	<0.0005	-	-
Bi	*mg/l*	0.001	<0.001	<0.001	<0.001	<0.001	-	-
B	*mg/l*	0.01	0.17	0.29	0.09	0.11	-	500
Cd	*mg/l*	0.0001	0.0005	0.0008	0.0002	0.0003	-	0.5
Ca	*mg/l*	0.03	695	1006	118	138	-	-
Cl	*mg/l*	0.5	24.7	23.9	44.9	41.5	-	-
Cr	*mg/l*	0.0006	<0.0006	<0.0006	0.0073	0.0068	-	5.0
Co	*mg/l*	0.001	0.011	0.038	<0.001	<0.001	-	-
Cu	*mg/l*	0.0005	0.0339	0.0817	0.0019	0.0024	0.3	-
Fe	*mg/l*	0.01	0.1	1.17	0.03	0.03	3	-
F	*mg/l*	0.01	0.44	0.28	0.35	0.21	-	150
Li	*mg/l*	0.005	0.038	0.082	0.008	0.011	-	-
Mg	*mg/l*	0.02	24.6	82.1	0.11	0.02	-	-
Mn	*mg/l*	0.0005	3.310	9.584	0.0030	<0.0005	-	-
Hg	*mg/l*	0.00002	0.01876	0.01991	0.00009	<0.00002	-	0.1
Mo	*mg/l*	0.0005	0.0377	0.0096	0.0814	0.0904	-	-
Ni	*mg/l*	0.0005	0.0608	0.1277	0.0037	0.0054	0.5	-
P	*mg P/l*	0.01	0.02	0.01	<0.01	<0.01	-	-
Pb	*mg/l*	0.0005	0.0008	0.0169	<0.0005	<0.0005	0.2	5
K	*mg/l*	0.05	11.8	14.8	10.3	13.5	-	-
Se	*mg/l*	0.001	<0.001	0.001	0.002	0.002	-	1.0
Si	*mg/l*	0.01	35.4	56.1	2.40	1.94	-	-
Na	*mg/l*	0.05	N/A	25.3	18.3	21.3	-	-
S	*mg S/l*	0.01	107	109	198	203	-	-
Tl	*mg/l*	0.002	<0.002	<0.002	<0.002	<0.002	-	-
Ti	*mg/l*	0.01	0.35	0.5	0.11	0.13	-	-
U	*mg/l*	0.001	0.007	0.012	<0.001	<0.001	-	2
V	*mg/l*	0.0005	<0.0005	<0.0005	<0.0005	<0.0005	-	-
Zn	*mg/l*	0.001	0.027	0.063	<0.001	<0.001	0.5	-

[3] Quebec provincial water quality objectives (*Directive 019* - MDDELCC, 2012 – FE: final effluent; AI: Annex 2) http://www.mddelcc.gouv.qc.ca/milieu_ind/directive019/

3.3.2 Monolithic Leaching Tests (MLT)

Two MLT were performed for the CPB recipes made of 5 and 7% of Slag-GU 70-30. The following sections present the evolution of the physicochemical parameters (pH, Eh and conductivity), and the evolution of the concentrations and the cumulative loadings of elements. Note that the elements having lower concentrations than the ICP-AES limit detection are not presented below (e.g., As, Cd, Co, Cr, Cu, Ni, Pb); their dissemination is considered negligible under aerobic and saturated conditions.

3.3.2.1 Physicochemical parameters

Figures 1 to 5 present the evolution of the physicochemical parameters (i.e., pH, Eh, conductivity, acidity and alkalinity) of the water samples for the two MLT. In summary, the pH of the water samples is relatively high (≈ 10.6), the Eh varied from 200 mV to 600 mV and the electrical conductivity between 200 and 400 µS/cm. Acidity and alkalinity are constant at values close to 0.5 and 66 mg $CaCO_3$/l.

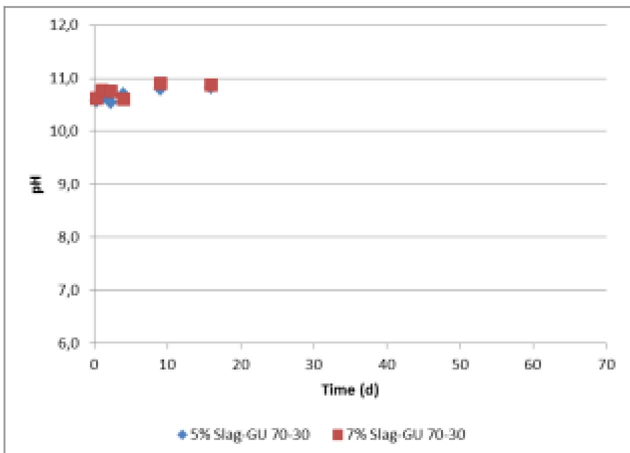

Figure 1: pH evolution of the MLT water samples

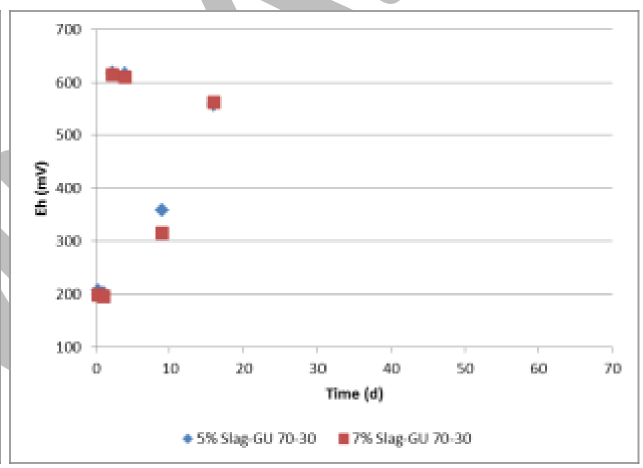

Figure 2: Eh evolution of the MLT water samples

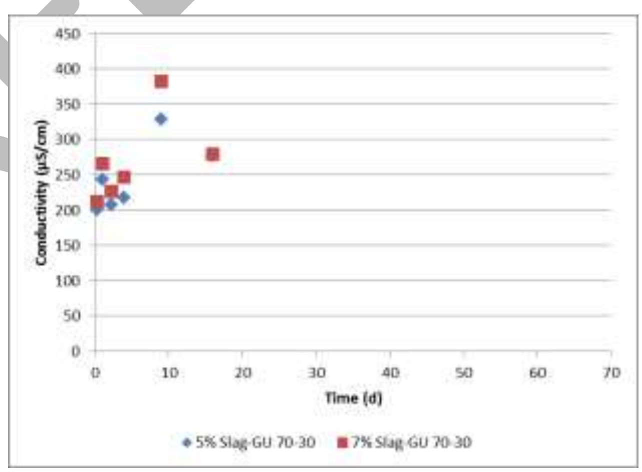

Figure 3: Electrical conductivity evolution of the MLT water samples

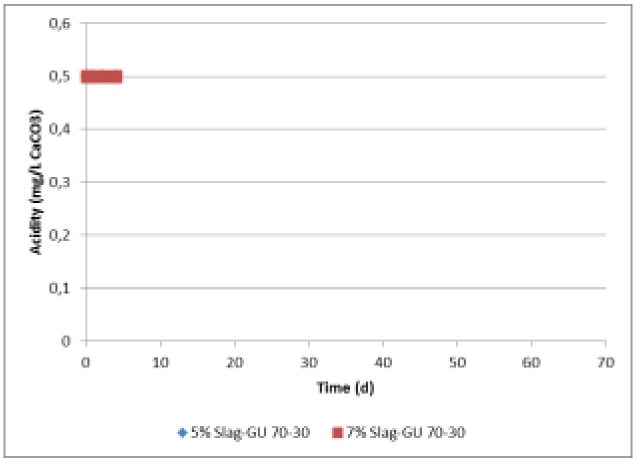

Figure 4: Acidity evolution of the MLT water samples

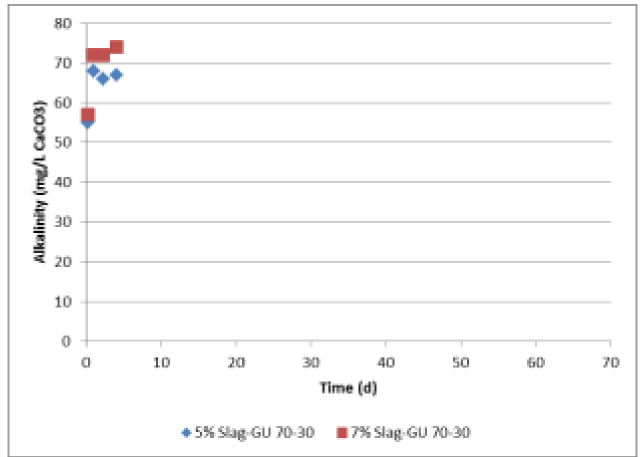

Figure 5: Alkalinity evolution of the MLT water samples

3.3.2.2 Concentrations and cumulative loadings

Figures 5 to 16 present the evolution of the concentrations and the cumulative loadings of elements having higher concentrations than the ICP-AES detection limit (dotted lines). Note that, the requirements defined by the Quebec *Directive 019* (MDDELCC, 2012) on the mining industry are presented for the concentrations of Fe and Zn (final effluent – red lines). It is important to recall that the concentrations of As, Cu, Ni and Pb were lower than the ICP-AES detection limit. More precisely:

- *Figure 6* shows higher concentrations of Al for the CPB made of 7% of Slag-GU 70-30; the dissolution and the relatively higher amount of aluminosilicate (i.e., muscovite – *table 3*) could explain this phenomenon. Note the same phenomenon is observed for the concentrations of K (*figure 10*) and Si (*figure 15*).
- The concentrations of Ba are relatively low and similar for the two MLT (*figure 7*).
- The concentrations of Ca are relatively higher for the CPB recipe made of 7% of Slag-GU 70-30 due to the higher binder content (*figure 8*).
- The concentrations of Fe (figure 9) are relatively low due to the low solubility of Fe and its slow dissolution kinetics at alkaline pH. No significant difference is observed between the two MLT.
- The concentrations of Mg (*figure 11*) and Mn (*figure 12*) are relatively negligible due to the low amounts of carbonates (i.e., magnesian calcite, dolomite – *table 3*).
- *Figure 13* shows higher concentrations of Na for the CPB made of 5% of Slag-GU 70-30; the dissolution and the relatively higher amount of sodium aluminosilicate (i.e., albite – *table 3*) could explain this phenomenon.
- The concentrations of S_{tot} are relatively similar for the two MLT. Note that the percentage of S_{tot} for the CPB recipe made of 5% Slag-GU 70-30 was higher (*table 4*).
- The concentrations of Zn are negligible (*figure 16*).

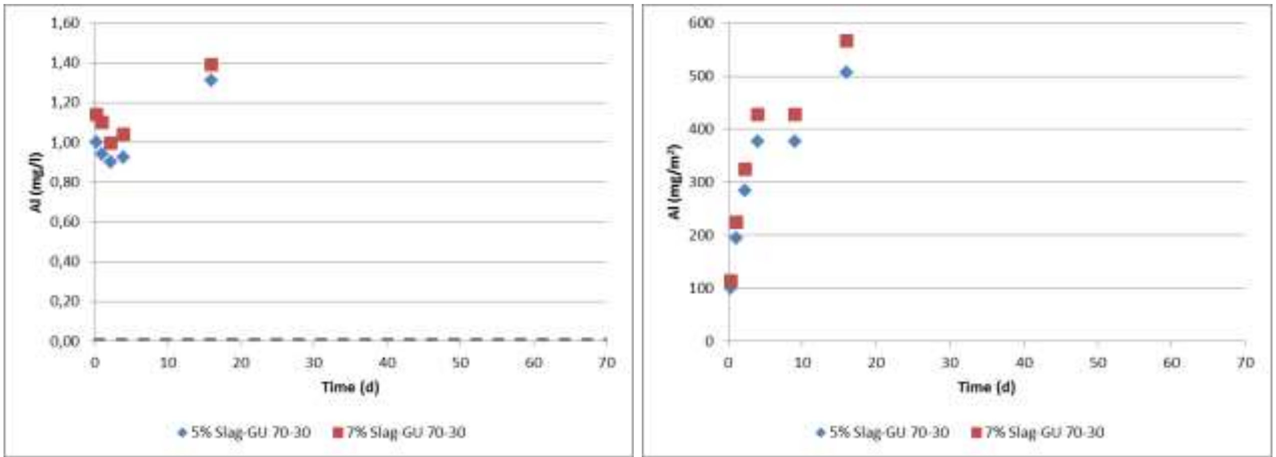

Figure 6: Evolution of Al concentrations and cumulative loadings for the MLT water samples

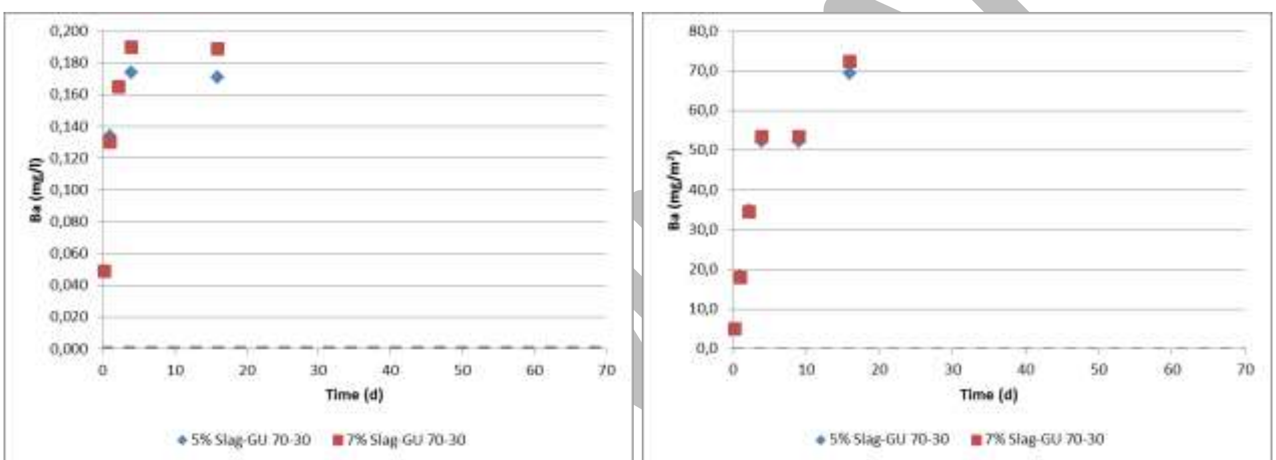

Figure 7: Evolution of Ba concentrations and cumulative loadings for the MLT water samples

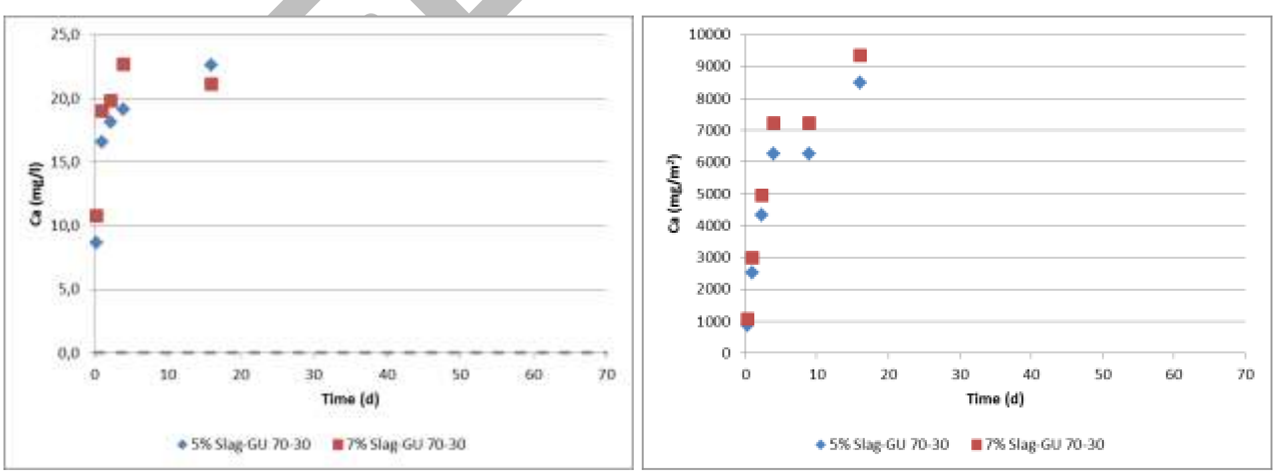

Figure 8: Evolution of Ca concentrations and cumulative loadings for the MLT water samples

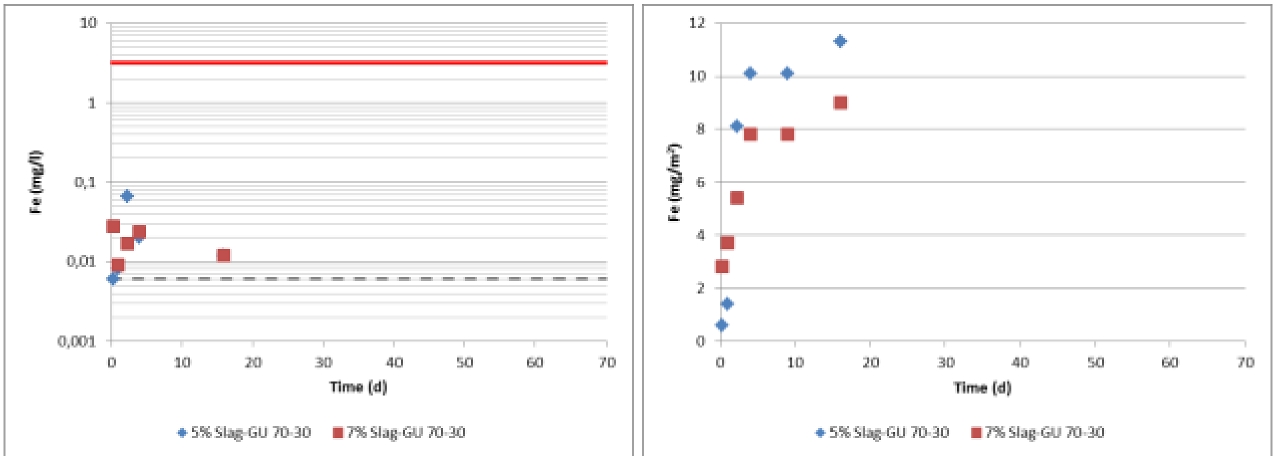

Figure 9: Evolution of Fe concentrations and cumulative loadings for the MLT water samples

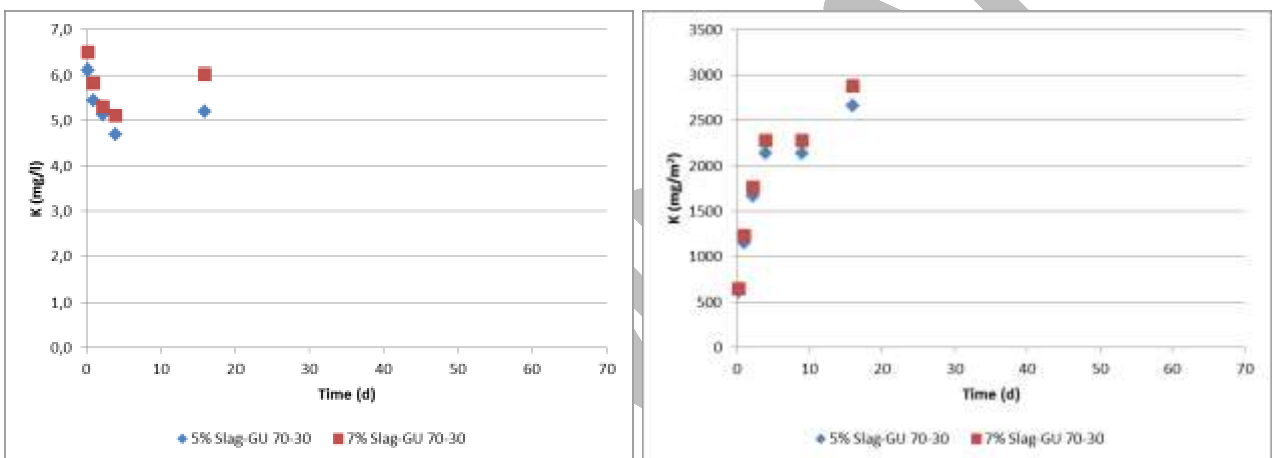

Figure 10: Evolution of K concentrations and cumulative loadings for the MLT water samples

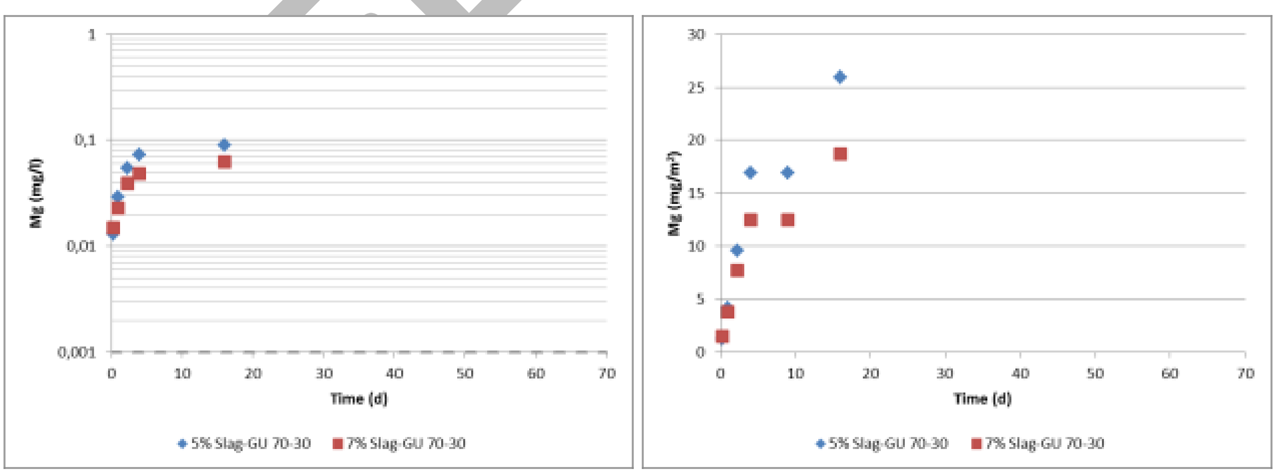

Figure 11: Evolution of Mg concentrations and cumulative loadings for the MLT water samples

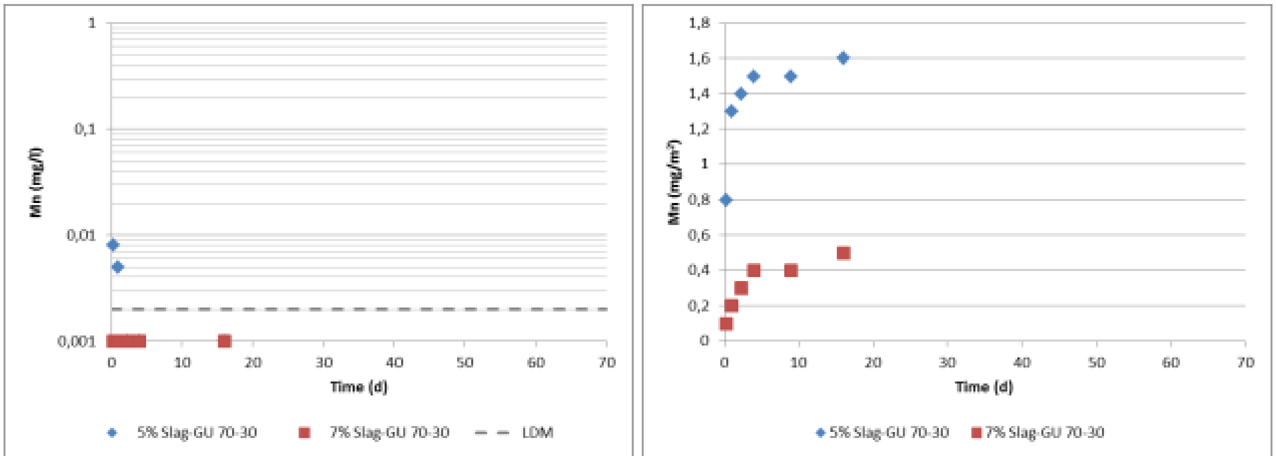

Figure 12: Evolution of Mn concentrations and cumulative loadings for the MLT water samples

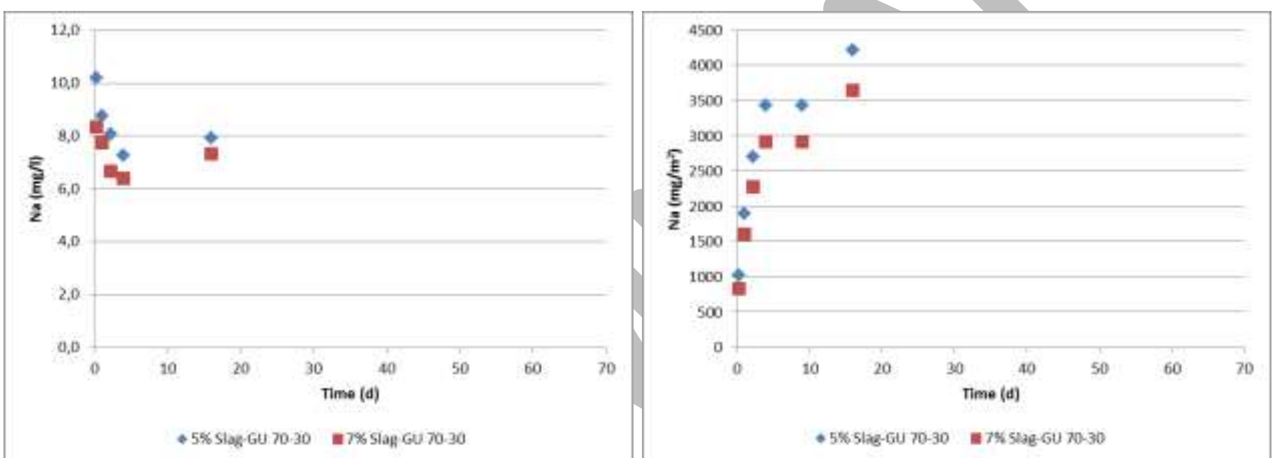

Figure 13: Evolution of Mg concentrations and cumulative loadings for the MLT water samples

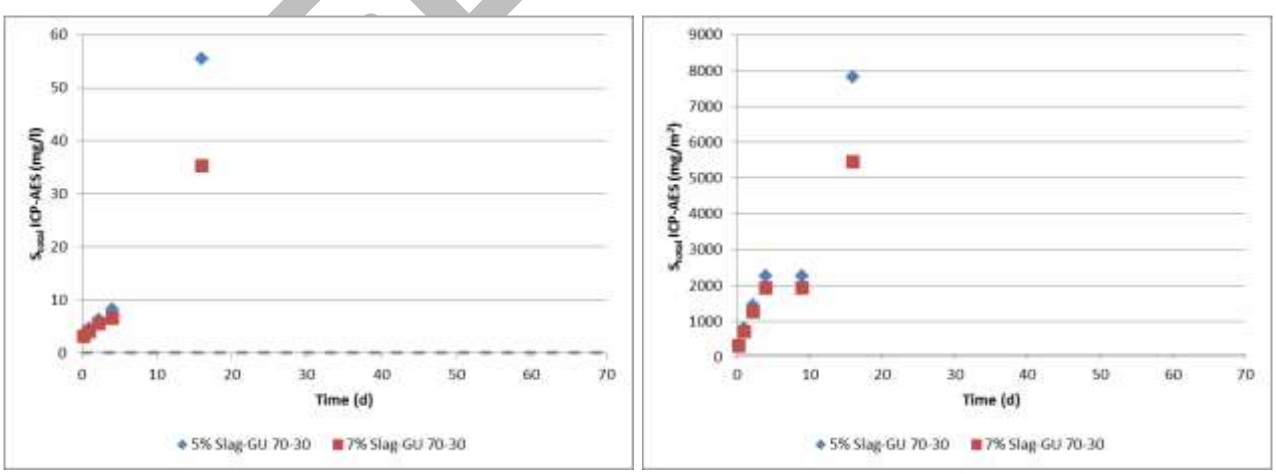

Figure 14: Evolution of S_{tot} concentrations and cumulative loadings for the MLT water samples

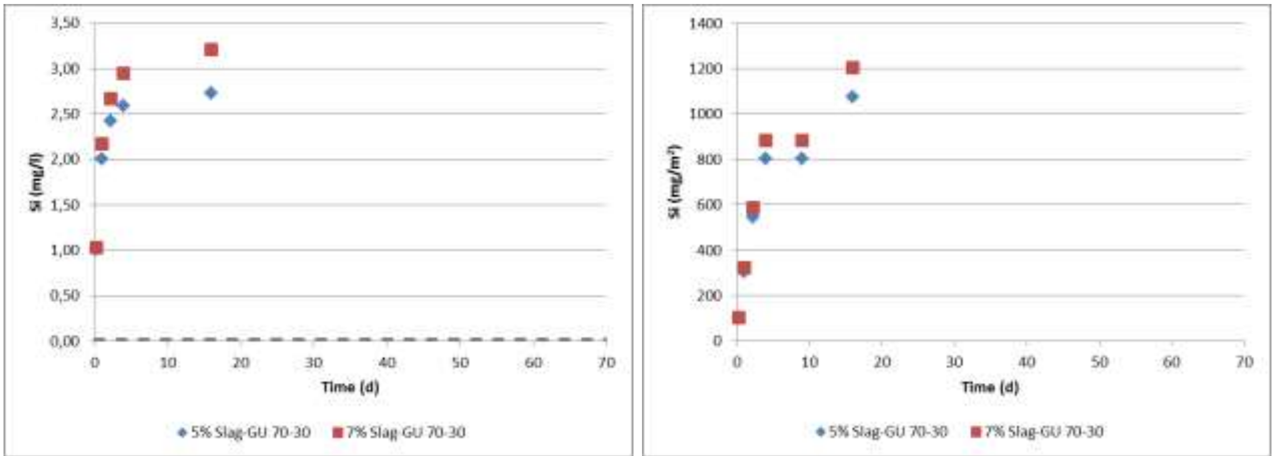

Figure 15: Evolution of Si concentrations and cumulative loadings for the MLT water samples

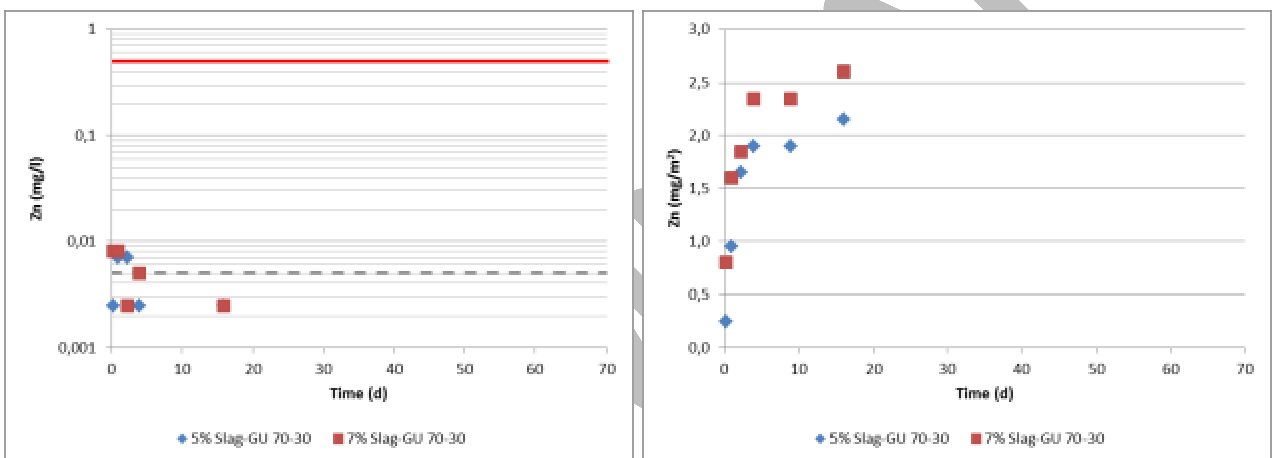

Figure 16: Evolution of Zn concentrations and cumulative loadings for the MLT water samples

In summary, the preliminary results show that the mobility of heavy metals and metalloids is relatively low for the two CPB recipes made of 5 and 7% of Slag-GU 70-30. In addition, there is no significant difference between the two MLT.

4. Conclusions

The objective of this study was to characterize two CPB recipes made of 5 and 7% of Slag-GU 70-30 and to evaluate their reactivity through SPLP-TCLP tests and Monolithic Leaching Tests. The results of the chemical and mineralogical characterization showed CPB with similar properties. In addition, the TCLP-SPLP tests and the MLT showed a low potential leachability of metals and metalloids for the two CPB recipes, which confirms a low reactivity. The preliminary results are in compliance with the requirements defined by the Quebec *Directive 019* on the mining industry.

Appendix 1

Analysis Certificates