

1 **ASSESSMENT OF THE COMBINED USE OF BASIC OXYGEN FURNACE**
2 **SLUDGE AND HYDROGEN PEROXIDE IN THE TREATMENT OF ACID**
3 **MINE DRAINAGE**

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14 Acknowledgments: The authors would like to thank Filipe A. T. Alves and Patricia Lopes at LAQ-
15 DEMET/UFMG for performing the ICP-OES analyses. The authors would also like to thank the Center of
16 Microscopy at University of the state of Minas Gerais (<http://www.microscopia.ufmg.br>) for providing
17 the equipment and technical support for the experiments involving water analysis and electron
18 microscopy; the Foundation of Support and Research of the state of Minas Gerais (FAPEMIG); the
19 Coordination of Superior Level Staff Improvement (CAPES) and the National Council for Scientific and
20 Technological Development (CNPq) for their support during this research.

21
22 ABSTRACT –We recently demonstrated the use of basic oxygen furnace sludge (BOFS) to remove
23 arsenic and sulfate from acidic solutions, which was found to be an interesting alternative for the reuse of
24 steel waste. In this study, four systems were evaluated to determine whether BOFS is stable in acidic
25 solutions and capable of removing As, Mn, and sulfate from acid mine drainage (AMD). In the S1 system
26 (BOFS/DEIONIZED WATER pH 2.5), the stability of the residue was evaluated by placing the BOFS in

27 deionized water acidified with H_2SO_4 until the pH reached 2.5. This system was maintained for 408 h
28 under agitation to evaluate the possible solubilization of metals present in the BOFS. The results showed
29 that only Ca and Mg were solubilized, and the pH increased from 2.5 to 12 after 408 h. The S3 system
30 (BOFS/AMD) evaluated the metal removal capacity by BOFS and achieved 100% removal of As and Mn
31 and 70% removal of sulfate after 648 h. In the first 30 min, the pH increased from 2.5 to 9.0, which was
32 maintained until the end of the experiment. Simultaneously, S4 and S5 systems (BOFS/AMD / H_2O_2)
33 were also evaluated using the oxidizing agent H_2O_2 (29% w/w) in the following proportions: 0.5 mM in
34 S4 and 1 mM in S5. The removal of As, Mn, and sulfate in these systems was similar to that in the S3
35 system, which contained only BOFS. The results demonstrated that the formation of iron oxides was not
36 accelerated by H_2O_2 and that iron, which is present in high concentrations in BOFS, was not the primary
37 agent influencing metal removal from AMD.

38 Keywords: basic oxygen furnace sludge (BOFS), steel waste reuse, arsenic removal, sulfate removal,
39 passive treatment

40

41 1. INTRODUCTION

42 Acid mine drainage (AMD) presents serious environmental pollution problems due to its high acidity and
43 high concentrations of As^{3+} , As^{5+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , $\text{Fe}^{2+}/\text{Fe}^{3+}$, and Cd^{2+} ad sulfate (Skousen et al.
44 2000). Because of its corrosive nature, AMD interacts with rocks, which contain different metals, thus
45 facilitating metal solubility. Hence, AMD can facilitate the accumulation of high concentrations of
46 dissolved metals in receiving waters and negatively affect biota (Kefeni et al. 2017).

47 Over the past 50 years, significant effort has been made to reduce the impact of AMD on the environment
48 by removing metals and sulfate via neutralization, primarily using industrial chemicals. The most popular
49 chemicals commonly used for neutralization include limestone (CaCO_3), hydrated lime ($\text{Ca}(\text{OH})_2$), and
50 lime (CaO). These processes collectively consume protons and produce alkalinity, thereby reducing the
51 impacts of AMD (Mayes et al. 2009).

52 Technologies that use zero valente iron (Fe^0 ; ZVI) have been successful in removing dissolved metals.
53 Corrosion products from Fe^0 such as $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, lepidocrocite ($\gamma\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$),
54 magnetite (Fe_3O_4), and hematite (Fe_2O_3) are important in the removal of various contaminants
55 (Satapanajaru et al. 2003) through adsorption and co-precipitation mechanisms. The formation of these

56 oxyhydroxides depends on the pH and availability of O₂ in the system. In the pH range of natural waters,
57 Fe²⁺ can hydrolyze and form Fe(OH)₂ on the surface of ZVI (Eq. 1). Fe²⁺ has limited stability and is
58 sensitive to the presence of molecular oxygen (O₂). The oxidation of Fe²⁺ species due to the presence of
59 O₂ is rapid, and the reaction rate increases as pH increases. Depending on the availability of O₂, various
60 oxyhydroxides such as Fe₃O₄, Fe(OH)₃, and FeOOH are generated (Eq. 2–4) (Guan et al. 2015).



65 The aging process of oxy-hydroxides is usually accompanied by dehydration and conversion in less
66 porous structures (Anderson and Benjamin 1985), leading to serious problems such as corrosive
67 passivation (loss of reactivity), i.e., the slow kinetics of Fe⁰ corrosion water and the subsequent low
68 efficiency to remove target contaminants (Guo et al. 2016). When the Fe⁰ surface is activated by
69 oxidizing agents such as KMnO₄, NaClO, and H₂O₂ (Guo et al. 2008, Guo et al. 2016, Li et al. 2018,
70 Yang et al. 2016), the oxidation process is continuous, thus increasing metal removal efficiency.
71 Iron-rich materials including Fe⁰, as alkaline industrial by-products that have been treated as waste, have
72 been studied recently for AMD remediation. The most common alkaline industrial products tested for
73 AMD treatments are cement kiln dust, lime kiln dust, red bauxite sludge, coal fly ash, and blast furnace
74 slag. By-products from quicklime manufacturing were used instead of commercial quicklime or slaked
75 lime, which are traditionally applied as neutralizing chemicals for AMD treatment (Tolonen et al. 2014).
76 The residual sludge produced by washing the gas system from the blast furnace slag as well as fine solid
77 particles recovered after the wet washing of gases generated from the basic oxygen furnace (BOF) are
78 known as residual gas sludge (BOFS). These types of sludge have been reported as among the most
79 effective materials for treating AMD (Jafaripour et al. 2015).

80 Recently, Araujo et al. (2019) proposed the use of BOFS to remove arsenic and sulfate in an acidic
81 solution (pH 2.5). It was found that although BOFS contains 50% Fe⁰, the primary mechanism for
82 removing arsenic and sulfate was calcium-mediated precipitation, with no species of As adsorbed or
83 precipitated in the form of iron oxy-hydroxides. According to the authors, the iron oxides present in the
84 system may not have been efficient in removing contaminants due to the formation of a passive layer of
85 iron oxides/hydroxides on the surface of the ZVI.

86 The objective of this study was to demonstrate the ability of BOFS in removing metals (As, Mn, and Mg)
87 and sulfate present in actual AMD and evaluate whether combining an oxidizing agent (H₂O₂) with BOFS
88 increases metal removal efficiency through the continuous oxidation of ZVI.

89 **2. MATERIALS AND METHODS**

90 *2.1 Characterization of BOFS*

91 BOFS was collected from a gas-washing system in a melt shop during steel production via an oxygen
92 converter or Linz–Donawitz (LD) process. Approximately 200 kg of BOFS was collected and divided
93 into 20-kg samples, which were dried on plates at 70 °C for 24 h. The samples were further separated into
94 50 g portions, which were sealed in plastic bags and stored in a dry place during the entire study period.
95 Chemical analyses of the BOFS were performed using aqua regia. In the aqua regia digestion method, the
96 sample was digested in concentrated acid (1:3 HNO₃/HCl) and, then, placed in a digester block for 2 h at
97 ~80 °C. The fused sample was, then, dissolved in a 10% v/v HNO₃ solution and analyzed by inductively
98 coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optima 7300DV) according to
99 the conditions described in Tables S1 and S2.

100 Total carbon and sulfur were determined using a LECO SC632 sulfur carbon. BOFS toxicity was
101 determined according to the Brazilian standard (ABNT 2004), which classifies solid waste according to
102 its toxicity. The crystalline phases were identified by X-ray diffraction (XRD) using a Rigaku
103 diffractometer (Geiger-Flex 2037) with radiation CuK α = 1,54051 Å. Scanning electron microscopy
104 (SEM) and energy dispersive spectroscopy (EDS) were performed using an FEI Quanta 200 field
105 emission gun scanning electron microscope. The identification and quantification of the iron phases
106 present in the BOFS were performed using Mossbauer spectroscopy in a conventional Mossbauer
107 spectrophotometer (constant acceleration, source of ⁵⁷Co in Rh matrix, using α -Fe as the standard). The
108 granulometry of the samples was analyzed by a laser diffraction particle size distribution analyzer (Horiba
109 LA-950).

110 *2.2 Characterization of aqueous samples*

111 AMD was collected from a gold mine in Minas Gerais, Brazil. The collected volume (200 L) was stored
112 in high-density polyethylene drums in a cold chamber until analysis. Deionized water was also
113 characterized and the results are shown in Table S3.

114 The pH electrode (HACH 2000) was calibrated using National Institute of Standards and Technology
 115 (NIST) traceable pH of 2.0, 4.0, 7.0, and 10.0 buffers and the oxidation-reduction potential (ORP)
 116 electrode (InLab Redox Ag with reference electrolyte 3 mol/L KNO₃; Mettler Toledo) reported in relation
 117 to the standard hydrogen electrode (SHE) which forms the basis of the thermodynamic scale of
 118 oxidation-reduction potentials (Langmuir 1971) and conductivity (Hanna HI 9835). Aqueous samples
 119 were analyzed using an inductively coupled mass spectrometer (ICP-OES)—Perkin Elmer Optima
 120 7300DV.

121 *2.3 Stability and removal of metals by BOFS and BOFS/H₂O₂ - batch tests*

122 The conditions proposed in each system are shown in Table 1.

123 **Table 1-** Evaluated systems containing BOFS

ID	System (S/L)*	BOFS (g)	Solution (mL)	Ratio S/L (g/L)	pH
S1	BOFS Deionized water	1	40	25:1	2.5
S3	BOFS AMD	1	40	125:1	2.5
S4	BOFS AMD	1	40	125:1	2.5
S5	BOFS AMD	1	40	125:1	2.5

124 *solid + liquid

125 *BOFS stability assessment - S1 system*

126 To assess the stability of BOFS in relation to the availability of metals in the medium, the S1 system
 127 (BOFS/DEIONIZED WATER pH 2.5) was monitored. Initially, 300 mL of deionized water with pH =
 128 6.3 was separated. Then, approximately 15 µL of H₂SO₄ (98% and 1.84 g.cm³) in 300 mL of water was
 129 added for S1, S3, S4, and S5 systems, resulting in an increase of 30 mg.L⁻¹ of sulfate in these systems.
 130 After these adjustments, the EH (0.67 mV) and electrical conductivity (4,94 mS.cm⁻¹) of the AMD were
 131 measured.

132 Subsequently, 1 g of BOFS and 40 mL of this acidified deionized water solution were transferred to each
 133 of the seven Falcon tubes of the S1 system, reaching a ratio of 25:1 S/L. Flasks were subjected to
 134 agitation (150–160 rpm) in a thermostated shaker at a temperature of ~25 ± 2 °C. Samples were collected
 135 at 0, 6, 24, 48, 144, 240, and 408 h for physical-chemical and arsenic and sulfate analyses. The T7 flask,
 136 corresponding to the experiment time (408 h) was also analyzed for Ca, Fe, Mn, Mg, and Na in ICP-OES.

137 *Evaluation of metal removal efficiency by AMD with oxidizing agent*

138 In this stage, three systems were analyzed: S3 (BOFS/AMD); S4 (BOFS/AMD/H₂O₂ 0.5 mM); and S5
139 (BOFS/AMD/H₂O₂ 1 mM) to which 5 g of BOFS in 40 mL of AMD was added in Falcon™ tubes. This
140 S/L ratio of 125 g : 1 L of BOFS and AMD is similar to the S/L ratios proposed in other studies
141 (Jafaripour et al. 2015; Masindi et al, 2018; Name and Sheridan, 2014). For S4 and S5 systems, H₂O₂
142 (29% p/p) was added to compare the efficiency with respect to the S3 system, which contained no
143 oxidizing agent. Considering that BOFS contains ~50% of ZVI in the S4 system, 10 µL H₂O₂ was added
144 at a ratio of 1 g : 0.5 mM ZVI/H₂O₂ (Guo et al. 2015, Guo et al. 2016). In the S5 system, 20 µL H₂O₂ was
145 added to evaluate a ratio of 1 g: 1 mM ZVI/H₂O₂. The peroxide volume was added above the BOFS
146 sample in Falcon™ tubes. The mixture was allowed to rest for 10 min to promote longer contact
147 between H₂O₂ and the BOFS; then, 40 mL was added to AMD in all tubes.

148 In a 2 L beaker were added 1500 mL of AMD, 7.5 mL of As (V) stock solution (1000 mg.L⁻¹) of As(V)
149 (Na₂HAsO₄.7H₂O) and 7.5 mL of As (III) (NaAsO₂). These reagents were added to enrich AMD with 10
150 mg.L⁻¹ of total As (As(V) + As(III)). Subsequently, this solution was transferred to the flasks of the S3,
151 S4, and S5 systems.

152 The closed Falcon™ tubes containing 5 g of BOFS and 40 mL of AMD remained under agitation (150–
153 160 rpm) in a thermostated shaker at a temperature of 25 ± 2 °C. At 0, 0.5, 1, 3, 6, 24, 72, 144, 216, 312,
154 480, and 648 h, the tubes corresponding to each time were removed for physical–chemical analysis of
155 arsenic and sulfate. The samples corresponding to the times T0, T2 (0.5 h), T4 (3 h), and T12 (648 h)
156 were also analyzed for Ca, Fe, Mn, Mg, and Na using ICP-OES.

157 *2.5 Geochemical modeling*

158 Based on the results of the physical-chemical characterization of the BOF solid phases, geochemical
159 modeling was performed before and after the experiments using the PHREEQC software (Parkhurst and
160 Appelo 1999). With the modeling, the speciation of the ions in solution and their ion activities, the
161 saturation indices of mineral phases, and the precipitations and physicochemical parameters of the solutions
162 were obtained. The experiments were modeled based on the chemical composition of AMD and the solid
163 phases observed in the BOF before and after the S3 and S5 experiments. The calculated contents of the
164 solids were divided into 50 equal parts and added sequentially to AMD. In the model, the phases found in
165 the BOF samples were inserted before and after the experiments. The modeling was performed in a closed
166 system as well as in the experiments.

167 2.6 *Quality assurance and quality control*

168 A Quality assurance and quality control (QA/QC) program has been established and implemented to
 169 guarantee reliable results. For liquid samples, quality control involved carrying out experiments in
 170 triplicate and publishing the data as mean values with standard deviations (SD). Data with a percentage
 171 difference (SD) of $\leq 10\%$ in triplicate or duplicate samples were considered acceptable. For solid
 172 samples, the quality was monitored using a certified reference material (NIST SRM 2710A; Montana II
 173 Soil) and the recovery with standard deviation (SD) $\leq 15\%$ was considered good. As an analytical quality
 174 control, “blanks” (analysis BLK) were inserted, which allowed for the measurement of values below the
 175 quantification limits (QL) of the method. Lutetium ($1 \text{ mg}\cdot\text{L}^{-1}$) was used as an internal standard element to
 176 monitor the effects of the matrix and the sensitivity deviations of the ICP-OES instrument.

177 **3. RESULTS AND DISCUSSION**

178 *3.1 Characterization of BOFS*

179 Results of the granulometric analysis of the 250-g sample of raw BOFS are presented based on the
 180 parameters for calculating the granulometric composition according to Wentworth (1922). Figure S1
 181 shows the percentages of the passing and granulometric curves. The results of the granulometric analyses
 182 showed that 95% of the material was below 0.52 mm, 50% below 0.21 mm, and 5% below 0.06 mm,
 183 which are considered fine sand.

184 Table 2 shows the percentage chemical composition of the main metals present in the BOFS and the
 185 certified material (CANMET Till-3). BOFS is mainly composed of Fe (84%), Ca (3%), and Si (1%). The
 186 concentrations of sulfur and carbon in the sample were 0.003% and 0.645%, respectively.

187 **Table 2** - Major and minor elements present in BOFS and certified material

% (p/p)									
Samples	Al	Ca	Fe	Mg	Mn	Na	P	Si	Ti
A1	<0.10	2.67	85.45	0.57	0.51	0.22	<0.05	0.90	<0.025
A2	<0.10	2.84	81.93	0.64	0.50	0.24	<0.05	0.98	<0.025
Average \pm SD	-	2,76 \pm 0,088	83,71 \pm 1,762	0,61 \pm 0,034	0,51 \pm 0,002	0,23 \pm 0,009	NA ⁽¹⁾	0,94 \pm 0,044	-
CANMET Till- 3									
Measured	7.33	1.43	3.09	1.08	0.04	2.53	<QL ⁽²⁾	32.54	0.30
Certified	6.46	1.88	3.05	1.03	0.05	1.96	0.05	32.30	0.29

Recovery (%)	114	76	101	104	70	129	-	101	102
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188 (1) not analyzed (2) quantification limit

189 BOFS characterization tests indicated that, according to NBR10004 (ABNT 2004), the waste originating
 190 from the crude BOFS sample is classified as Class I (hazardous) as it presents a reactive corrosive
 191 characteristic (pH 12.56). All other parameters analyzed showed adequate concentrations. The results are
 192 shown in the Supplementary Material.

193 Analysis of the diffraction lines revealed the presence of the following main constituent phases: calcite
 194 (CaCO_3), hematite (Fe_2O_3), wustite (FeO), iron (Fe), and magnesium oxide (MgO) (Fig. 1). Any other
 195 minor constituent phases are difficult to identify because of the complexity of the diffractograms and the
 196 low intensity of their diffraction lines. The main peaks of CaCO_3 were 2θ : 36 ($d = 3.04 \text{ \AA}$), 47 ($d = 1.92$
 197 \AA), and 39 ($d = 2.28 \text{ \AA}$); those of Fe^0 were observed at 2θ : 45 ($d = 2.02 \text{ \AA}$), 65 ($d = 1.43 \text{ \AA}$), and 85 ($d =$
 198 1.17 \AA) and those of FeO were observed at 2θ : 42 ($d = 2.15 \text{ \AA}$), 32 ($d = 2.47 \text{ \AA}$), and 61 ($d = 1.51 \text{ \AA}$).

199

200 **Fig. 1** – XRD patterns of raw BOFS

201

202 These results were confirmed by the Mossbauer spectrum (Figure S2), which provides, among other
 203 things, information about the structural, electrical, and magnetic properties of a solid, in this case, for the
 204 ^{57}Fe isotope. According to Goldanskii and Herber (1968), nuclear hyperfine interactions are disturbances
 205 that occur in the energy levels of the nucleus due to nuclear interactions and electrical and magnetic fields
 206 in the vicinity of the nucleus. Thus, it is possible to obtain the isomeric displacement (δ ; mm/s) the
 207 quadrupolar unfolding (Δ/ε ; mm/s) and from them, the iron fraction corresponds to the relative area for
 208 each of the iron oxidation states (Table 3). Of the total iron in the sample, it was identified that 48%
 209 corresponded to metallic iron (Fe^0), 41% to wustite (FeO), and 11% may be part of maghemite ($\gamma\text{-Fe}_2\text{O}_3$)
 210 and ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$).

211 **Table 3** - Hyperfine parameters of paramagnetic sites of Mossbauer spectra adjustments for raw BOFS
 212 samples. Complementary results are presented in Table S4

Sample	Oxidation state	δ (mm/s) \pm (0.05 mm/s)	Δ/ε (mm/s) \pm (0.05 mm/s)	Relative area \pm (1 %)
RAW BOFS	Fe^0	0.0	0.0	48
	Fe^{2+} (FeO)	1.06	0.83	41

Fe^{3+} ($\gamma\text{-Fe}_2\text{O}_3$)	0.20	0.47	11
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213

214 The Mossbauer analyses performed for the precipitates of the S3 (BOFS/AMD) and S5
 215 (BOFS/AMD/H₂O₂ 1 mM) systems as well as the Mossbauer results for the raw BOFS sample are shown
 216 in Fig. 2. It is observed that the iron oxidation sequence has been extended, resulting in hematite
 217 formation: $\alpha\text{-Fe}$ (Fe^0) \rightarrow FeO (wustite) \rightarrow $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) \rightarrow $\alpha\text{-Fe}_2\text{O}_3$ (hematite).

218

219 **Fig. 2** - Percentage of iron phases for raw BOFS, BOFS after reaction with AMD (S3), BOFS after
 220 reaction with AMD (S3), and BOFS after reaction with AMD/H₂O₂ 1 mM (S5) by Mossbauer

221

222 Comparing the results of the percentage of Fe phases (Fig. 2) between the solid samples obtained after the
 223 tests of the BOFS + AMD and BOFS + AMD + H₂O₂ systems, it was observed that at the end of the
 224 experiment, both the $\alpha\text{-Fe}_2\text{O}_3$ fraction and the $\gamma\text{-Fe}_2\text{O}_3$ (hematite) fraction in the BOFS + AMD system
 225 were higher than those in the system containing H₂O₂. This finding indicates that there was continuous
 226 oxidation of elemental Fe in the system containing an oxidizing agent, maintaining it primarily in the
 227 form of iron oxide (wustite–FeO).

228 3.2 Characterization of aqueous samples

229 Both the deionized water used in the S1 system and the AMD used in S3, S4, and S5 systems had a pH of
 230 ~6. To acidify them to a pH 2.5, ~50 μL H₂SO₄ (98% and 1.84 g.cm³) in 1000 mL was added to S1, S3,
 231 S4, and S5 systems, resulting in an increase of 30 mg.L⁻¹ of sulfate in these systems. After these
 232 adjustments, both the Eh and the conductivity were measured in AMD, obtaining the values of 0.67 mV
 233 and 4.94 mS.cm⁻¹ respectively. After the analysis of AMD by ICP-OES (Table 4), a low concentration of
 234 As was observed. AMD was, then, added with 10 mg.L⁻¹ of As.

235 **Table 4** - Chemical characterization of AMD (ICP-OES)

Parameter	Ag	Al	As	Au	Ca	Cd	Co	Cr	Cu	Fe
Conc. (mg.L ⁻¹)	<0.25	<2.5	<1.0*	<0.25	497.06	<0.1	<0.1	<0.1	<0.1	10.20
Parameter	Mg	Mn	Na	Ni	Pb	S	Sb	Sn	Ti	Zn
Conc. (mg.L ⁻¹)	755.92	5.49	68.34	<0.1	<0.25	1586.55	<0.1	<0.25	<0.25	<1.0

236 3.3 Metals removal by BOFS and BOFS/H₂O₂ - batch tests

237 BOFS stability assessment – S1 system

238 The graphs in Fig. 3 show that the initial pH (2.5) of the S1 system (BOFS/DEIONIZED WATER pH
239 2.5) increased to 11.4 after 24 h until the end of the experiment (408 h).

240

241 **Fig. 3** - Variations of pH, Eh, conductivity, and Total Arsenic (As T) in the S1 system (BOFS/DEIONIZED
242 WATER pH 2.5)

243

244 The increase in pH was due to the calcium carbonate contained in BOFS. The process of neutralizing an
245 acidic solution by dissolving CaCO₃ is quick and can be described by Eq. 5 at low pH values and by Eq. 6
246 with higher pH values (Blowes et al. 2003). Under alkaline conditions at a pH of ~10, the reaction shown
247 in Eq. 7 prevails.



248 It was observed that at the beginning of the experiment the redox potential (Eh) started at ~800 mV and
249 during the first 6 h, it decreased to ~400 mV and remained stable until the end of the experiment. This
250 behavior is expected because the consumption of protons, through the mechanism presented in Eq. 5 and
251 Eq. 6, causes the pH to increase and the Eh value to decrease. Considering the atmospheric pressure of 1
252 atm, the increase in pH and consequent decrease in Eh is consistent with the Nernst equation: $E_H =$
253 -0.0591 pH . The low conductivity (750 μS) of the S1 system confirms the low presence of ions in the
254 solution at the end of the experiment (T 408 h). Among the parameters analyzed (Ca, Fe, Mg, and Mn),
255 only Ca (10% p/v) was solubilized into the medium, with a concentration of 78.1 $\text{mg}\cdot\text{L}^{-1}$. Fe, Mg (1.25
256 $\text{mg}\cdot\text{L}^{-1}$), and Mn (0.05 $\text{mg}\cdot\text{L}^{-1}$) were below the QL (quantification limit) at the end of the experiment.
257 Sulfate was also below the QL throughout the monitoring period. Fig. 4 shows the Mössbauer analyses
258 for raw BOFS and BOFS/DEIONIZED WATER pH 2.5 (S1 system). These analyses confirm the

259 oxidation of the Fe phases: Fe⁰ and Fe²⁺ (magnetite) clearly showed an increase in the Fe³⁺ (hematite)
260 phase.

261

262 **Fig. 4** - Percentage of the iron phases for raw BOFS and BOFS / DEIONIZED WATER pH 2.5 of the S1
263 system after 408 h

264

265 *Evaluation of metal removal efficiency from AMD with oxidizing agent in S3, S4, and S5 systems*

266 The graphs of the physical–chemical parameter results (Fig. 5), demonstrate a similar behavior among S3
267 (BOFS/AMD), S4 (BOFS/AMD/H₂O₂ 0.5 mM), and S5 (BOFS/AMD/H₂O₂ 1 mM) in relation to pH, Eh,
268 and conductivity parameters, mainly in S4 and S5 systems, which differ only in the concentration of
269 peroxide used.

270

271 **Fig. 5** - Variations in pH, Eh, conductivity, As, and sulfate in the samples of S3, S4, and S5 systems

272

273 In view of the physicochemical results of pH and Eh, it was observed that the systems simultaneously
274 achieved balance after 0.5 h, with a slight variation in the final pH and Eh of the S3 system compared to
275 the others. The electrical conductivity (CE) remained constant from 0.5. to 72 h, decreasing until all
276 systems reached a value of ~2 mS.cm⁻¹ in 648 h. The removal of As in the S3, S4, and S5 systems was
277 95%, resulting in the final concentration < QL (0.5 mg · mg.L⁻¹), and the removal of sulfate was 60%–
278 70% (final concentration = 1400–1900 mg. L⁻¹), resulting in a higher concentration than the maximum
279 value allowed by Brazilian legislation in surface waters (250 mg.L⁻¹).

280 Regarding the removal percentage, there were no significant differences among S3 (BOFS/AMD), S4
281 (BOFS/AMD/H₂O₂ 0.5 mM), and S5 (BOFS/AMD/H₂O₂ 1 mM) systems, as shown in Fig. 6. Considering
282 the lack of significant difference in the kinetics of S4 and S5 systems, for which only the H₂O₂
283 concentration differs, the removal of other metals (Ca, Fe, Mg, and Mn) was evaluated at the following
284 time intervals: T0; T1 (0.5 h), T3 (3 h), and T12 (648 h).

285

286 **Fig. 6** - Concentration (mg.L⁻¹) of Ca (A), Fe (B), Mg (C), and Mn (D) in S3 and S5 systems

287

288 It is observed that, on average, 700 mg.L⁻¹ of Ca remained in the S3 and S5 systems. In relation to Fe,
289 after 3 hours of experiment, all quantifiable Fe precipitated in both the S3 and S5 systems. This proved
290 that the presence of H₂O₂ in the S5 system delayed the precipitation of Fe, but did not make the system
291 more efficient in removing contaminants. In the S3 system, the concentration of soluble iron was
292 considerably low since the beginning of the experiment. In the S5 system, as the pH of the solution
293 remained low until 0.5 h, precipitation of the sulfate in the form of ferric sulfate and of ferrous sulfate
294 may have occurred.

295 Studies carried out by Pantuzzo et al. (2008) proved that the As precipitation or sorption mechanism in
296 the form of amorphous ferric arsenate (FeAsO₄·2H₂O), with the same molecular formula as the
297 scorodite, is unfavorable in alkaline conditions, being favored in the pH range 1.5–4.0. Laboratory
298 experiments conducted by Langmuir et al. (2006) using a solution rich in arsenic from uranium mining
299 yielded the same results. In these experiments, the solution was neutralized from pH 2 to pH 8 with the
300 addition of Ca(OH)₂. A small amount of crystalline scorodite ($K_{ps} = 10^{-25,83}$ mol.L⁻¹) precipitated at a pH
301 close to 2 and amorphous iron arsenate ($K_{ps} = 10^{-23}$ mol.L⁻¹) precipitated at a pH between 2 and 3. The
302 removal of arsenic during neutralization can be explained by assuming precipitation of 90%–98% of As
303 (V) as scorodite when pH = 2–3; the adsorption of the remaining As (V) by a precipitate as amorphous
304 iron arsenate occurs between a pH of 2.18 and 7.37. Although the As (V) removal mechanism remains
305 unknown, our results indicate that it is irreversible. This pH acid condition is maintained for a short time
306 in the studied systems, considering that within 30 min the pH becomes ~12. Considering the pH and EH
307 conditions that formed in the system (high pH and oxidizing environment) and the solubility product of
308 ferric arsenate ($K_{ps} = 10^{-24}$ mol.L⁻¹) and calcium arsenate ($K_{ps} = 10^{-19}$ mol.L⁻¹), the thermodynamic
309 conditions in the system favor species stability. The behaviors of Mg and Mn in both systems were
310 similar, and at the end of the experiment, the concentration of soluble species reached values lower than
311 the QL of the method.

312 *3.4 Geochemical modeling*

313 The modeling of the experiments was performed by PHREEQC using the database
314 PHREEQC_ThermoddemV1.10_06Jun2017.dat (Blanc et al. 2012). The BOFS mass used in the
315 experiments (5 g) was divided into 50 equal fractions (0.1 g each) and these fractions were added
316 gradually to 40 mL of the solutions in experiments S3 (BOFS) and S5 (BOFS + H₂O₂) (see Materials and
317 Methods for further details). Under these conditions, the geochemical modeling reproduced the physical-
318 chemical conditions (Fig. 7-A) and obtained the same experimental results observed at 648th h of
319 incubation. From the 20th addition of the 2g of BOFS in both models (Fig. 7-B), the ion concentrations in
320 solution (Ca²⁺, SO₄²⁻, Mn²⁺, As³⁺, and As⁵⁺) and the precipitations of crystalline and amorphous
321 compounds were observed in the experiments (Fig. 7-C). This means that only 2 g of the BOFS reacted in
322 both experiments; however, in the modeling, other results would be achieved if the system reached
323 chemical equilibrium, especially in relation to pH, which is a little higher in the modeling.

324 Fig. 7-A shows the reduction in EH, which can be explained by the oxidation of Fe⁰ (releasing electrons
325 into the system) and FeO together with the formation of Fe₂O₃ (hematite) and Mn²⁺Fe₂³⁺O₄ (jacobsite)
326 (Fig. 7-C). Gypsum (CaSO₄·2H₂O) precipitation occurred since the beginning of the addition of BOFS in
327 the solutions. Before the addition of BOFS, the gypsum saturation index in the AMD (saturation index
328 (SI) = 0.03) indicated that the DAM was initially in equilibrium with gypsum. The solubilization of
329 calcite, present in the BOFS added to the system, provided the Ca²⁺ necessary for the precipitation of
330 sulfate in the form of gypsum. With the pH stabilized at ~10 after the addition of 0.3 g of BOFS, brucite
331 (Mg(OH)₂) precipitation began (Fig. 7-C). The pH was stabilized around 10 until the addition of 2g of
332 BOF. The precipitation of Ca₅(AsO₄)₃OH, which started with the addition of 1.5 g of BOF, must have
333 been controlled by competition with the gypsum for Ca²⁺ available in solution. With the gypsum
334 precipitation since the beginning of the experiment, there was a decrease in the sulfate available for
335 gypsum formation, thereby facilitating the precipitation of Ca₅(AsO₄)₃OH. After the precipitation of
336 Ca₅(AsO₄)₃OH, the concentration of dissolved Ca²⁺ remained constant in the solution; there was no
337 further dissolution of the added calcite until BOFS addition was complete. Thus, from the beginning of
338 the experiment, the precipitation of gypsum inhibited the removal of As until the SO₄²⁻ in the solution was
339 consumed and the saturation/precipitation of the gypsum was reduced.

340 The solubility of Mg was controlled by the precipitation of brucite, which removed Mg almost entirely.
341 With the termination of brucite and Ca₅(AsO₄)₃OH precipitations (Fig. 7-C) after the addition of 2 g of
342 BOFS, OH⁻ consumption decreased, which allowed the pH to increase in both systems in the modeling

343 with the continued addition of BOFS up to 5 g (Fig. 7-A). Mn was removed after the addition of 1.75 g of
344 BOFS (Fig. 7-A) as a result of jacobsite ($\text{Mn}^{2+}\text{Fe}_2^{3+}\text{O}_4$) precipitation in S3 and S5 systems, under stable
345 pH and Eh conditions (Figs. 7-B and 7-C).

346 This suggests that the precipitation of jacobsite was controlled by the availability of Fe^{2+} in solution. This
347 was the only phase containing Mn identified in the modeling capable of removing Mn from the solution
348 in experiments S3 and S5. In modeling, the reduction in Eh is ascribed to the continued oxidation of the
349 Fe phases.

350 **Fig. 7** – Graphical representation of the conditions proposed in the modeling by PHREEQC using
351 PHREEQC_ThermmodemV1.10_06Jun2017.dat database (Blanc et al. 2012)

352 The mineralogical composition of the XRD patterns of (A) raw BOFS, (B) BOFS/AMD, and (C)
353 BOFS/AMD/ H_2O_2 1 mM are shown in Fig. 8, confirming the species observed in geochemical modeling.
354 The main peaks of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were 2θ : 11.67 ($d = 7.57 \text{ \AA}$) and 20.8 ($d = 4.27 \text{ \AA}$). For $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$
355 (johnbaumite), the peaks were observed at 2θ : 31 ($d = 2.86 \text{ \AA}$) and 32 ($d = 2.78 \text{ \AA}$) (Bothe and Brown
356 1999, Zhu et al. 2006).

357

358
359 **Fig. 8** – XRD patterns of (A) raw BOFS, (B) BOFS/AMD, and (C) BOFS/AMD/ H_2O_2 1 mM

360

361 The majority of elements present in the S1 system (BOFS/AMD) were also detected by SEM with EDS
362 (Fig. 9). Figure S3 show the morphological properties of BOFS and BOFS after contact with AMD and
363 H_2O_2 obtained by SEM image corresponding chemical mappings by EDS. It was observed that the slag
364 resulting from the S3 system (BOFS/AMD) has a leaf and rod-shaped structures. S5 system particles
365 contained spherical aggregates of irregular shapes with coral reef-like structures. The surface of these
366 forms is smooth, representing a typical crystalline form of gypsum (CaSO_4). Similar results were reported
367 by Du et al. (2016). The resulting residue was compact, indicating that the material formed was
368 crystalline. The spherical structures indicate the iron particles and the aggregates of small particles of
369 varying sizes and shapes, such as stems, leaves, reefs, and bulky nodules, indicating the formation of new
370 precipitates (Masindi et al. 2017).

371

372 **Fig. 9** –SEM image of (A) BOFS (2000x) and (B) BOFS (20000x). Highlighted area indicates where EDS
373 was analyzed. (C, D, E, F) Corresponding chemical mappings obtained by EDS

374

375 CONCLUSIONS

376 This study showed that a BOFS can be an economical alternative to treat acid mine drainage with high
377 arsenic and sulfate. The precipitation of arsenic in the form of calcium arsenate ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$) and
378 having a low solubility constant ($K_{\text{sp}} = 6.8 \times 10^{-19} \text{ mol.L}^{-1}$), suggests the stability of this compound, thus
379 simplifying the disposal of this compound. residue after use.

380 Despite being rich in metallic iron (ZVI) and iron oxyhydroxides, as shown in the characterization by
381 XRD, SEM and Mossbauer, the experiments and geochemical modeling in PHREEQC proved that iron
382 compounds were not the main source of removal of contaminants. The use of the oxidizing agent (H_2O_2)
383 and BOFS to favor the formation of iron oxy-hydroxides did not exceed the removal rate achieved by the
384 system that contained only BOFS. The concentration of calcium carbonate (CaCO_3) was sufficient to
385 raise the pH from 2.5 to pH 10 and remove 100% As and 70% sulfate. In addition to these contaminants,
386 there was also total removal of Mg, Mn, and Fe. This study also found that BOFS has the potential to
387 neutralize AMD's acidity and mitigate the toxic effects of these chemical compounds.

388 A disadvantage of this proposal is that the remaining sulfate concentration is still high and, in the case of
389 disposal of this effluent directly into a watercourse, it may compromise the quality of the water intended
390 for human consumption, whose limit is 250 mg.L^{-1} of sulfate. This means that a technology for polishing
391 this effluent must be associated with the process.

392 DECLARATIONS

393 Ethics approval and consent to participate: No applicable

394 Consent for publication: No applicable

395 Availability of data and materials: The datasets used and/or analysed during the current study are
396 available from the corresponding author on reasonable request.

397 Competing interests: The authors declare that they have no competing interests.

398 Funding: This work was supported by the Foundation of Support and Research of the state of Minas
399 Gerais (FAPEMIG), the Coordination of Superior Level Staff Improvement (CAPES) and the National
400 Council for Scientific and Technological Development (CNPq). The funding sources were not involved in
401 study design, nor the collection, analysis, and interpretation of data, nor in the writing of the report, nor in
402 the decision to submit the article for publication.

403 Authors' contributions: study conception and design - S. F. Araujo, V. S.T. Ciminelli and C. L. Caldeira;
404 assays execution - S. F. Araujo and J. P. Rodrigues; analysis - S. F. Araujo, J. P. Rodrigues; V. S.T.
405 Ciminelli and C. L. Caldeira; results interpretation and writing - S. F. Araujo, V. S.T. Ciminelli, C. L.
406 Caldeira, G. F. Simões and R. P. Borba. All authors contributed to interpretation of results and manuscript
407 revision. All authors read and approved the final manuscript.

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