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1 **EFFECT OF LOCAL MATERIALS ON THE SILVER SORPTION AND STRENGTH**
2 **OF CERAMIC WATER FILTERS**

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8

9 **ABSTRACT**

10 In this paper, we present a systematic evaluation of the effects of local clays and the
11 manufacturing process on the performance of ceramic water filters (CWFs) impregnated with
12 silver compounds, which are used for point-of-use water treatment in developing countries.
13 Mineral composition, silver sorption/desorption, and strength are the important characteristics
14 that influence effectiveness and durability of CWFs during transport and use. Laboratory tests
15 were conducted on ceramic samples obtained from five CWF factories around the world to
16 determine their mineral composition, silver sorption/desorption, and flexural strength. The
17 results of this study showed that clays that contain traces of crystalline albite or crystalline
18 pyroxene have better sorption of silver species than those that do not. The results showed that
19 the Freundlich model provided the best fit for both ionic silver and silver nanoparticles for all of
20 the ceramic materials that were tested. Thus, this model can be used to optimize the
21 manufacturing process and the application of silver. Silver nanoparticles were desorbed more
22 slowly than ionic silver, so they last longer in the ceramic material. Water that contains a high
23 concentration of divalent ions is not recommended for preparing solutions of silver nanoparticles
24 due to aggregation of the particles, which limits their sorption by the ceramic materials. In this
25 study, the mineralogy of the source materials was found to have the most significant influence on
26 the strength of ceramic filters.

27 Keywords: mineral composition, silver, sorption, desorption, flexural strength

28

29 **1. INTRODUCTION**

30

31 Ceramic water filters (CWFs) impregnated with silver nanoparticles were developed in
32 Guatemala by Dr. Fernando Mazariegos with the support of the World Bank and the Inter-
33 American Bank. Dr. Mazariegos' work involved the evaluation of ten models of low-cost,
34 domestic water filters. In response to Hurricane Mitch in 1999, Potters for Peace used CWFs as
35 a sustainable water treatment technology in Nicaragua [1]. At present, there are more than 30
36 established ceramic filter manufacturing facilities in 20 countries that produce about 40,000
37 filters per month [1]. These silver-impregnated CWFs are easy to use, requiring little training for
38 the users, and they are produced locally and require no additional chemicals for operation.

39 Ceramic filters are manufactured by pressing and firing a mixture of clay and a
40 combustible material, such as flour, rice husks, or sawdust, prior to treatment with silver
41 nanoparticles. The filters are formed using a filter press, after which they are air-dried and fired
42 in a flat-top kiln, in which the temperature is increased gradually to about 900 °C over an eight-
43 hour period. This forms the ceramic material and combusts the sawdust, flour, or rice husks in
44 the filters, making it porous and permeable to water [1]. After firing, the filters are cooled and
45 impregnated with a silver solution (either silver nanoparticles or silver nitrate) by painting it onto
46 the filters or dipping the filters in a bath of the solution. It has been demonstrated that the silver
47 solution adds disinfectant properties to the CWF, thereby decreasing the bacteria concentration
48 and increasing the quality of the water.

49 Ionic silver and silver nanoparticles are used extensively for their medicinal and
50 disinfectant properties [2-7]. It has been demonstrated that silver ions produce reactive oxygen
51 species (ROS) by proxy [8], prevent the replication of DNA, and affect the permeability and

52 structure of the cell membrane [9]. Similarly, silver nanoparticles have different anti-microbial
53 mechanisms, including (i) interactions with the surface of the cell membrane, creating “pits” and
54 affecting permeability, (ii) the release silver ions that penetrate the cell and interrupt the
55 replication of DNA, and (iii) the production of ROS.

56 Both silver salts and nanoparticles are added to CWFs in three different ways, i.e., by
57 painting them onto the filter, dipping the filter in a silver solution, and mixing the silver with
58 clay, sawdust, and water in a powder form. One survey found that 33% of the factories painted
59 the silver solution onto the CWFs, 56% dipped the CWFs into the silver solution, and the
60 remaining 11% mixed the silver in powdered form with clay and sawdust [1]. About 83% of
61 factories used silver nanoparticles, and 17% used silver nitrate [1].

62 Previous studies of CWFs showed that increasing the concentration of silver added to the
63 CWFs increased the removal of pathogens [10-12]. The current average amount of silver added
64 to CWFs is about 0.003 mg Ag/g ceramic. No study has assessed the possibility of obtaining a
65 higher sorption of silver species by the ceramic material while minimizing desorption. The rate
66 of desorption of silver from CWFs has been determined in field and laboratory studies [12, 13],
67 but no studies have been performed to evaluate the influence of the type of clay, accessory
68 minerals, and the concentration of silver added to the ceramic materials.

69 The strength of CWFs also is an important factor because it is related to the durability of
70 the filters during transport and use. CWFs are unreinforced, so the strength of the filters depends
71 largely on the tensile strength of the ceramic material used to make the filter. Recent studies by
72 Plapally et al. [14] indicated that clay mineralogy and the combustible material (e.g., sawdust
73 and rice husks) used in manufacturing CWFs affect the pore distribution and hence the strength
74 of the ceramic materials. In this study, we performed a fracture toughness test on single-edged,

75 notched, bend specimens from different sections of CWFs that were manufactured under
76 controlled conditions in the laboratory. The roles of process variables, such as the ratio of clay to
77 combustible material, the firing program, and the way the materials are handled during the
78 manufacturing process, are still somewhat uncertain.

79 The objective of this study was to investigate the influence of local clay materials
80 and the manufacturing process on silver sorption/desorption and the strength characteristics of
81 CWFs. The specific hypothesis to be tested is that the silver sorption capacity and strength
82 properties of CWFs can be predicted based on the distribution of the minerals in the clay used to
83 make the CWFs.

84 **2. TESTING PROCEDURES**

85
86 Ceramic samples were obtained from CWF factories located in the United States (A),
87 Guatemala (B), Ghana (C), Peru (D), and Nicaragua (E). These samples were representative of a
88 wide variety of clay types and manufacturing methods. None of the CWFs had silver added to
89 them during the manufacturing process.

90 **2.1. Bulk Mineralogy and Chemistry**

91 The ceramic samples were pulverized using a porcelain mortar and pestle, and the
92 pulverized material was passed through a 150-micron sieve and placed in the sample cell of a
93 Terra X-ray diffraction and fluorescence unit manufactured by InXitu, Inc. Samples were
94 analyzed for at least 50 exposures to the X-ray. Dominant XRD peaks were compared with
95 standard reference profiles for known minerals using X Powder software
96 (<http://www.xpowder.com/>). Bulk chemistry data, collected during the same analysis, yielded
97 low-resolution detection of the selected metals.

98 **2.2. Porosity**

99 Porosity is defined as the ratio of the volume of voids (V_v) to the total volume (V_t). Thus,
100 it is a measure of the void space in a material. The ceramic materials were dried at 105 °C until
101 they reached a constant weight. This weight was recorded as W_o , and then the ceramic materials
102 were immersed in water for 24 h. Then they were weighed again, and this weight was recorded
103 as W_f . With the voids still full of water, the ceramic materials were covered in parafilm and
104 placed in a graduated cylinder with a known volume of water, recorded as V_o . Then, the final
105 volume of water after the addition of the ceramic material was recorded as V_f . The porosity (n)
106 was determined using the following equation:

$$107 \quad n(\%) = \frac{V_v}{V_t} = \frac{(W_f - W_o)}{(V_f - V_o)} \times 100 \quad (1)$$

108

109 **2.3. Sorption/Desorption of Silver Species**

110 Silver nanoparticles were obtained from Laboratorios Argenol SL in Spain (Collargol
111 70.37% silver content). The nanoparticles manufactured by Laboratorios Argenol were
112 synthesized by irradiation techniques and stabilized using casein. This is the most common
113 source of silver nanoparticles used by CWF factories. Ionic silver was obtained in the form of
114 silver nitrate (AgNO_3) from Sigma-Aldrich (> 99.999% purity).

115 Concentrations of ionic silver were determined using a Thermo-Scientific Orion
116 9616BNWP ion-Plus Sure-Flow Silver/Sulfide probe. The concentration of silver nanoparticles
117 in solution was obtained using ICP-OES (X series, Thermo Elemental); with this method, we are
118 able to detect the total silver in solution, i.e., the combination of silver nanoparticles and ionic
119 silver.

120 The experiments were conducted at similar conditions of ionic strength (I) using 0.00147
121 I of KNO_3 (1.9 mM KNO_3) and 0.00147 I of $\text{Ca}(\text{NO}_3)_2$ (0.48 mM $\text{Ca}(\text{NO}_3)_2$), which represented
122 monovalent and divalent electrolytes, respectively. A dynamic light scattering (DLS) system was
123 used to determine the sizes and distributions of the particles in the different electrolyte solutions
124 that were prepared. Malvern Zetasizer Nanoseries ZS90 was used to determine the zeta potential
125 of the silver nanoparticles at the different water chemistry conditions used in the experiments.
126 The characterization methodologies were described by the authors of previously-published work
127 [7, 15].

128 Batch sorption experiments for each silver specie on each of the five CWF materials using
129 either monovalent or divalent electrolyte solutions, were performed by combining the sorbent,
130 the aqueous silver solution, and organic-free, deionized (DI) water in 15-mL polypropylene
131 tubes. The mass of sorbent (ceramic material) used in each isotherm experiment was 5 g with a
132 total sample volume of 1 cm³. The aqueous silver solutions were prepared at concentrations of 10
133 g/L Ag^+ (AgNO_3) and 4.0 g/L Ag^0 . These concentrations and sorbent masses were used to
134 ensure that 30% to 90% of the silver species were sorbed at equilibrium. The aqueous silver
135 solution was mixed with DI water prior to contacting the ceramic materials at different ratios.
136 Tubes containing the diluted silver solution and no ceramic were also included in the experiment
137 and analyzed to determine the losses due to contact with the tubes or caps. No significant losses
138 were measured, and recovery in all tubes was determined to be greater than 98%. The difference
139 between the initial and final (equilibrium) mass of silver in the aqueous phase was considered to
140 be equal to that sorbed by the solid phase.

141 The data were fitted by two well-known models, i.e., the Langmuir and Freundlich
142 models. The Langmuir adsorption isotherm was used to describe the equilibrium between the

143 surface and the solution as a reversible chemical equilibrium between species. The surface of the
 144 adsorbent was made up of fixed individual sites at which molecules of the adsorbate could be
 145 chemically bound. We assumed that the reaction had a fixed free energy change for all sites and
 146 that each site was capable of binding, at most, one molecule of adsorbate. This assumes, at most,
 147 a monolayer of adsorbate on the adsorbent. (35)

148 To model the Langmuir Isotherm, the data were plotted as $\frac{C_A}{q_A}$ versus C_A , which resulted in
 149 a straight line with a slope of $\frac{1}{Q_M}$ and an intercept of $\frac{1}{b_A \cdot Q_M}$. Linear regression was used to
 150 determine the best fit parameters and the Langmuir regression parameters, Q_M and b_A , where Q_M
 151 is the maximum adsorbent-phase concentration of sorbate when the surface sites are saturated
 152 with sorbate, $\left(\frac{mg \text{ sorbate}}{g \text{ sorbent}}\right)$, and b_A is the Langmuir adsorption constant of the sorbate, $\left(\frac{L}{mg}\right)$.

153 $\left| \frac{C_A}{q_A} = \frac{1}{b_A \cdot Q_M} + \frac{C_A}{Q_M} \right. \quad (2)$

154

155 The Freundlich adsorption isotherm was used to describe the data for heterogeneous
 156 adsorbents, such as activated carbon. Heterogeneous adsorbents often have varying site energies
 157 and are best described using the Freundlich isotherm. The Freundlich Sorption Equilibrium
 158 Model was derived as an empirical equation. It describes the equilibrium for heterogeneous
 159 sorbents and is the most frequently-used isotherm for activated carbon. To model the
 160 Freundlich isotherm, the data were plotted as $\log(q_A)$ versus $\log(C_A)$, using an equation that
 161 results in a straight line with a slope of $\frac{1}{n}$ and an intercept of $\log(K)$. The term $\frac{1}{n}$ is the
 162 Freundlich sorption intensity parameter (unitless). K is the Freundlich sorption
 163 capacity parameter, $\left(\frac{mg}{g}\right) \cdot \left(\frac{L}{mg}\right)^{\left(\frac{1}{n}\right)}$.

164 $\log(q_A) = \log(K) + \left(\frac{1}{n}\right) \cdot \log(C_A)$ (3)

165 Desorption experiments were conducted to determine the amount of sorbate (silver
166 species) that was desorbed from the sorbent (ceramic materials). After the sorption experiments,
167 the ceramic materials were dried in an oven at 25 °C for 24 h. This temperature was chosen to
168 simulate the incubator temperatures for both sorption and desorption agitating and the
169 temperature of the drying process used at the filter manufacturing factories. Then, the ceramics
170 were immersed in a vial that contained a background solution with the same background ions as
171 the sorption experiment. The vials were rotated in a rotating tumbler for 24 h at 25 rpm at 25 °C.
172 Equilibrium concentrations were measured at the completion of this period. Following this, the
173 ceramic materials were removed from the vials and dried in an oven at 25 °C for 24 h. This
174 procedure was performed twice for each sample of ceramic material.

175 **2.4. Strength**

176 Flexural strength was determined using the three-point bending test (ASTM C1161-02c)
177 that is commonly used in testing high-strength ceramic materials. A band saw was used to cut
178 small beams from pieces of the CWFs, and the tests were performed on these small beams. It
179 was only possible to perform the test on ceramic materials A, B, and E due to the lack of
180 appropriate materials shipped from the other factories. It was not feasible to obtain specimens
181 that had dimensions that were in exact accordance with ASTM specifications. Thus, for this
182 study, the height and length of the beams were 1 and 4.5 cm, respectively. The depth of the
183 beams was established by the wall thickness of the CWFs (which ranged from 1.5 to 2 cm), so
184 trimming was done only to obtain the necessary width and length. Therefore, trimming did not
185 influence the top or bottom surfaces of the beam, because any changes in these surfaces could
186 have affected the strength of the beam. Figure 1 shows the three different orientations of the

187 beams that were cut from the sides of the CWFs. The different orientations were used to
188 investigate possible strength anisotropy in the ceramic material associated with the
189 manufacturing process. Specimens trimmed from the bottom of the CWFs were tested in the z-
190 direction from the inside out.

191 The following equations were used to calculate flexural stress (σ_f) and flexural strain (ϵ_f),
192 respectively,[16]:

193

$$\sigma_f = \frac{3PL}{2wd^2} \quad (4)$$

194

$$\epsilon_f = \frac{6Dd}{L^2} \quad (5)$$

195

196 ,
197 where P is the load applied to the beam at midspan, L is the length of the span, w is the width of
198 the beam, d is the depth of the beam, and D is the displacement where P is located. The load was
199 applied at a constant displacement rate of 0.005 in/min using a Karol Warner Model 76 Load
200 Frame with a load cell that had a 50-lb capacity. Displacement was calculated by multiplying the
201 specified strain rate by the elapsed time. Equation 2 was used to determine the strength at the
202 maximum applied load.

203
204 **3. RESULTS**

205
206 **3.1. Bulk mineralogy and geochemistry**

207 *Mineralogy and Geochemistry via simultaneous XRD/XRF*

208 Ceramic samples from the United States (A), Guatemala (B), Ghana (C), Peru (D), and
209 Nicaragua (E) were analyzed under the same conditions. The ceramic sample from Nicaragua
210 was exceptional in its high background noise, indicating poor crystallinity, which was possibly
211 due to heavy erosion of the source material or additional milling of the ceramic components prior

212 to assembling the CWFs. Overlapping mineral contents in the fired ceramic material showed that
213 all of the samples except the Nicaraguan samples, had a quartz-dominated matrix (Table 1).
214 Differing amounts of the smectite group of clays occurred in the samples from the U.S.,
215 Guatemala, Peru, and, possibly, Nicaragua. Illite was detected in the samples from Peru and
216 Nicaragua. Samples from Guatemala and Peru contained pyroxene grains, which are common in
217 mafic volcanic rocks. The samples from Peru and Nicaragua contained albitic grains, which are
218 commonly found in weathered volcanic terrains. The samples from Ghana were exceptional in
219 that they were essentially all quartz. Note that the smectite group of clays has expandable
220 interlayer spaces, so the clays can accommodate interlayer water or large cations, according to
221 convention (Figure S1 in supplemental information).

222 **3.2. Porosity**

223 Porosity is the measure of interconnected voids in the ceramic material. The maximum
224 porosity measured, i.e., 48%, was for the CWFs made in Ghana, and the minimum porosity,
225 i.e., 40%, was measured for the CWFs made in the U.S. Table S1 (supplemental information)
226 shows the porosities that were measured for the ceramic materials used in the experiments.

227 Many studies have found that the range of porosity for CFWs manufactured in different
228 countries is between 35% and 44% [1]. Our results fell near the upper limit of the range. This
229 discrepancy with previous studies could be have been caused by the differences in the analytical
230 techniques used to determine porosity; we used a water intrusion method instead of the mercury
231 porosimetry that was used in other studies [13].

232 **3.3. Properties of the silver nanoparticles**

233 Figure 2 shows the mean size of the nanoparticles as a function of the type of electrolyte
234 used. As the calcium concentration increased, the mean size of the nanoparticle aggregates

235 increased up to 500 nm. When sodium was used as background ions, the largest size of the
236 aggregates was only 100 nm. The influence of the background electrolytes on the aggregation
237 kinetics of silver nanoparticles was reported previously by several authors with similar results as
238 those obtained in this study [7, 15, 17-19]. The aggregation of the nanoparticles could limit the
239 penetration of the particles to pores smaller than the size of the aggregate, thereby reducing the
240 amount of silver taken up by the ceramic material.

241 The zeta potentials of the silver nanoparticles for $\text{Ca}(\text{NO}_3)_2$ and KNO_3 water conditions
242 were -23.95 and -18.55 mV, respectively. The results implied that the nanoparticles were more
243 stable with 200 mg/L KNO_3 as the background solution than they were in the solution that
244 contained $\text{Ca}(\text{NO}_3)_2$. All of the nanoparticles had negative zeta potentials.

245 **3.4. Sorption of silver compounds**

246 **3.4.1. Silver Nanoparticles**

247 Figure 3 shows isotherm results of the batch silver nanoparticles for all the ceramic
248 materials at the different conditions of water chemistry. The isotherm data fitted both the
249 Langmuir isotherm and the Freundlich isotherm for the sorption of the silver nanoparticles. The
250 best fit was chosen by the R^2 values. The Freundlich isotherm provided the best fit for the range
251 of concentrations of silver nanoparticles sorbed by the ceramic materials at all water-chemistry
252 conditions that were tested. However, the R^2 values were much higher when potassium nitrate
253 was used, indicating a much better fit than that for calcium nitrate. Table 2 shows the fitting
254 parameters. From the fitting of the experimental results, it could be inferred that there was no
255 limit to the amount silver nanoparticles that can be sorbed by the ceramic materials, but, in
256 reality, we know that such a limit exists; we just could not determine what it was at the
257 experimental conditions used in this study.

258

259 **3.4.2. Ionic Silver**

260 Figure 4 shows the isotherms for all of the ceramic materials at the different water
261 chemistry conditions that were tested. Both Langmuir and Freundlich models fit the isotherm
262 data for silver ion sorption (data not shown). However, the Freundlich fit produced higher R^2
263 values than the Langmuir fit, so the former was selected as the better fit for the tested range of
264 concentrations of silver ions as sorbed by the ceramic materials in all water-chemistry cases.
265 There is one case for which the Freundlich model did not provide the better fit, i.e., 1, ceramic
266 materials from Guatemala with a background solution of calcium nitrate. However, the R^2
267 values for both isotherm fits were greater than 0.9, indicating a good fit for both the Freundlich
268 and Langmuir models. Table 2 shows details of the parameters used to obtain the fits of the
269 Freundlich and Langmuir models.

270 **3.5. Desorption**

271 **3.5.1. Silver Nanoparticles**

272 Figure 5(a) shows the average desorption per ceramic material for the two solutions. The
273 highest desorption with KNO_3 was for ceramic material from Ghana, which had an average
274 desorption of $0.41\% \pm 0.3\%$, and the lowest desorption was for the ceramic material from
275 Guatemala, with an average that was below our detection limit. The highest desorption with
276 $Ca(NO_3)_2$ occurred in the ceramic material from Ghana, which had an average of $1.92\% \pm$
277 1.02% , and the lowest desorption occurred in the ceramic material from Guatemala, which had
278 an average of $0.12\% \pm 0.09\%$. For all the ceramic materials tested, higher desorption values were
279 obtained when $Ca(NO_3)_2$ was used. This difference could have been caused by the particle size
280 of the aggregated nanoparticles. Large aggregates formed in the calcium solutions may not be
281 effectively trapped in the porous matrix of the ceramic material, so they may be desorbed easily.

282 These results are relevant to the manufacture of CWFs in the different countries, since the water-
283 chemistry conditions used to prepare the silver solution used to coat the CWFs in each location
284 could differ significantly. Factories that use groundwater, which usually has high concentrations
285 of divalent salts, to produce the nano-suspension of silver nanoparticles will produce CWFs that
286 release more silver nanoparticles to the treated water in comparison with factories that use
287 surface water with its low concentrations of divalent salts.

288 **3.5.2. Ionic Silver**

289 Figure 5(b) shows the total average desorption per ceramic material for the two water
290 quality conditions. The maximum desorption with KNO_3 occurred with the ceramic material
291 from Nicaragua, with an average of $44.54\% \pm 27.57\%$, and the minimum occurred with the
292 ceramic material from Guatemala, with an average of $6.40\% \pm 4.18\%$. The highest desorption
293 with $\text{Ca}(\text{NO}_3)_2$ occurred with the ceramic material from Ghana, with an average of $12.06\% \pm$
294 6.30% , and the minimum occurred with the ceramic material from Guatemala, with an average
295 of $5.67\% \pm 2.73\%$.

296 **3.6. Strength**

297 Figure 6 shows typical stress-strain curves from the sides of three different sources in the
298 inside-out (+R) loading direction. As the figure shows, the stress-strain behavior is almost linear,
299 eventually reaching a brittle failure at strains between about 1% and 3%. The strengths
300 calculated from the flexural tests are summarized in Figure 7.

301 Independent of the loading direction, the ceramic material from Nicaragua had the
302 highest flexural strength (> 500 psi), and USA sample had the lowest (<150 psi). Ceramic
303 material from Guatemala was slightly weaker than that from Nicaragua. To investigate the
304 possible reasons for the difference in strength, the strengths in the +R direction were plotted

305 versus effective porosity in Figure 8. As shown in the figure, the strength increases with an
306 increase in effective porosity, an unexpected behavior. A more porous material should have more
307 void space and thus have higher stresses in the ceramic matrix, resulting in a lower strength.
308 Therefore, the differences in strength are expected to be primarily due to differences in the
309 mineralogy of the clay, which could affect the bonding between particles. However, surface
310 imperfections induced by the manufacturing process may also have an effect.

311 The manufacturing process appears to produce a material that has the same strength on
312 the sides as it does on the bottom. This is shown by comparing the strengths measured from the
313 sides on the inside-out loading condition (+R) with the inside-out bottom strengths (Z). For
314 example, ceramic B showed 423 psi (sides) versus 440 psi (bottom), and sample E showed 528
315 psi (sides) versus 510 psi (bottom).

316 The orientation of the specimens on the sides had some effect on the measured strength,
317 suggesting minimal strength anisotropy. The effect was lowest in ceramic E which had a
318 maximum difference of 10 psi (2%) for an average strength of 524 psi. The anisotropy was more
319 pronounced in ceramic A, which had differences of 20 psi (23%) from the average strength of
320 132 psi. Also, the material appears to be the strongest when it is loaded from the outside-in (-R)
321 direction rather than the inside-out (+R) direction. However, this may be more attributable to the
322 curvature of the beam than to anisotropy. The -R loading direction has a beam that is concave
323 down (Figure 1), which produces more of an arch structure that would tend to result in more
324 compressive stresses than tensile stresses, making the material appear to be stronger.

325

326 **4. DISCUSSION**

327

328 Quartz and smectite-group clay minerals were present in all of the ceramic materials
329 studied; chemical differences (not assessed here) in the smectite-group clay fraction may be
330 partially responsible for the different sorption behaviors. Ceramic materials from Guatemala and
331 Peru were able to sorb greater amounts of silver nanoparticles; these ceramic materials contain
332 accessory pyroxene ($R_2Si_2O_6$, where R is an available cation, usually Mg^{2+} , Fe^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} ,
333 Ti^{3+} , Mn^{3+} , Na^+ , K^+ , or Li^+), and they contain albitic plagioclase feldspar ($NaAlSi_3O_8$) [20], so
334 they may have an overall negative surface charge. This may concentrate protons or available
335 cations on the surfaces of the mineral, localizing a patchy, positive charge distribution that would
336 attract the moderately-negative silver nanoparticles. There are several well-known examples of
337 surface charges existing on the surfaces of silicate minerals in response to pH-dependent ion
338 exchange and sorption processes, particularly when H^+ and OH^- interact with surficial ions [21].
339 In the cases of pyroxene and albite, the negative charges that are fundamental to their silicate
340 structure are likely controlling sorption behavior. More generally, H^+ and OH^- sorption also has
341 been observed in the case of zeolite minerals [22], especially in albites [23].

342 Regarding the silver nanoparticles used in this study, both their sizes and charges were
343 similar to those of citrate-capped nanoparticles, which are the nanoparticles that are most
344 commonly used in nanoproducts. In previous studies performed by one of the authors [15], it was
345 shown that casein-capped silver nanoparticles have greater stability the capping agents that have
346 lower molecular weights. It was also found that the dissolution of casein-capped nanoparticles
347 was below 0.5% of the total mass of silver added, so it was expected that the experimental
348 conditions used in this study would have resulted in a similar dissolution rate.

349 Ceramic materials from Ghana and the U.S. sorbed the least amount; these two materials
350 have simple mineral profiles, consisting of just quartz and smectite-group clays, respectively.

351 The Nicaraguan ceramic material presented an intermediate case, i.e., sorption properties were
352 intermediate when compared to the high-sorption Guatemala/Peru group and the low-sorption
353 Ghana/U.S. group. XRD data for the Nicaraguan ceramic material suggest the presence of trace
354 albite and pyroxene a lower overall crystallinity, as observed in high background in the XRD
355 results. When potassium nitrate was used as the background solution, high levels of sorption
356 occurred, the use of calcium nitrate as the background solution resulted in significantly less
357 sorption. The importance of the detection of albitic feldspar and pyroxene in the mineral profiles
358 of the ceramic materials that were tested may be as follows. First, the surfaces of natural mineral
359 grains are not regular; in fact, they are quite heterogeneous, with dissolution and reactivity of
360 surface phases dependent on their fine structures, including step and kink features [24]. Second,
361 feldspars are tectosilicate minerals with a three-dimensional array of linked SiO_4 and AlO_4
362 tetrahedra, with interstices that can host K, Na, Ca, or Ba in electroneutral arrangements [20].
363 Pyroxenes are inosilicates (i.e., chain silicates) composed of linked SiO_4 tetrahedra, each sharing
364 two O atoms with the neighboring tetrahedron. Available cations link the tetrahedral chains
365 together in pyroxenes, yielding a diverse cation (“R” in mineral formula above) budget for this
366 mineral, although, typically, it is dominated by Fe and Mg. R-O bonds typically are weaker than
367 Si-O bonds in silicate minerals, and natural specimens cleave along these weaker bond planes
368 (Huang, 1989); the resulting natural mixtures of pyroxene grains may have broken R-O bonds at
369 the edges, which may participate more readily in sorption. Indeed, cation exchange and
370 stoichiometric surface dissolution of pyroxene grains are well supported [25]. Although these
371 silicate minerals comprise only a small fraction of the total material, they may provide reactive
372 surfaces for the ionic and silver nanoparticles in experimental systems.

373 When potassium nitrate was used as the background solution, the ceramic material from
374 Guatemala sorbed the most ionic silver (followed by Peru), and the ceramic material from
375 Nicaragua sorbed the least. When calcium nitrate was used as the background solution, the
376 ceramic material from Guatemala sorbed the most ionic silver (followed by Peru), and the
377 ceramic material from Ghana sorbed the least. Ceramic materials from Guatemala and Peru
378 contain silicate mineral components (pyroxene or albite), and we propose that these components
379 contributed to the greater sorption capacity of metal ions, as discussed above. These results
380 indicated that the mineralogy of the ceramic material and the water chemistry of the background
381 solutions are important variables to consider when predicting the sorption of ionic silver by
382 ceramic materials.

383 Steep slopes in the coefficient (or when $1/n$ is close to 1) indicated high adsorptive
384 capacity at high equilibrium concentrations, but it diminished rapidly at lower equilibrium
385 concentrations. When the slope is relatively flat (or $1/n$ is much less than 1), it indicates that the
386 sorption capacity is not influenced significantly by lower equilibrium concentrations [26]. The
387 value of K can be taken as a relative indicator of the adsorptive capacity, and $1/n$ is indicative of
388 the energy or intensity of the reaction [27]. The Freundlich isotherm describes multilayer
389 adsorption, and it is not restricted to the formation of the monolayer, as is the Langmuir
390 isotherm.

391 Similarly, the model that fit the silver nanoparticles' sorption isotherm indicated that
392 silver ions seem to exhibit a very high sorption capacity on the ceramic materials. The maximum
393 saturation threshold was not achieved at the experimental conditions used in this study. It was
394 impractical to attain the high concentration required to achieve the threshold in the case of silver
395 nitrate, and aggregation issues associated with the silver nanoparticles precluded achieving it in

396 their case as well. It should be noticed that it was not possible to determine the composition of
397 the silver solution inside the pores of the ceramic materials at the end of the sorption test.
398 Therefore, it is possible that some silver still remained in solution (silver nitrate) or suspended
399 (silver nanoparticles) inside the pores and were not necessarily truly sorbed. The average pore
400 volume of the ceramic material was close to 0.5 cm^3 , and the mass of silver in the pore space
401 could be up to 5 mg at the highest equilibrium concentration obtained, indicating that less than
402 12% of the total silver was sorbed.

403 Transport of silver nanoparticles with similar physicochemical characteristics through
404 ceramic manufactured with industrial grade clay have been previously determine in continuous
405 systems [28].. This study showed that most of the desorption happen during the first 200min of
406 the test. In our batch mode experiments we observed that most of the detachment occurred
407 during the first desorption stage.

408 The desorption tests of silver compounds from the ceramic materials clearly showed the
409 advantage of the use of silver nanoparticles instead of silver ions as an anti-biofouling agent on
410 CWFs. Silver ions desorbed to an extent that was almost an order of magnitude greater than that
411 of the silver nanoparticles. This fact has two main implications, i.e., (i) large losses of chemicals
412 will occur if silver ions are used and (ii) more rinses will be required for CFWs impregnated with
413 silver ions in order to achieve the U.S. Environmental Protection Agency's standard for silver in
414 drinking water of 0.1 mg/L [29]. It also should be noted that the oral reference dose for silver is
415 0.005 mg/kg/day, so high concentrations of silver in treated water would exceed this standard,
416 and this is especially of concern when one considers children under the age of five, who
417 comprise one of the most important target populations of this technology.

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419 **5. CONCLUSIONS**

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422 The composition of clay seems to play an important role in the sorption of silver species.

423 The ceramic materials that contained pyroxenes had better sorption of silver, resulting in
424 enhanced performance relative to the removal of pathogens from the water. Also, this finding
425 could allow local manufacturers of CWFs to improve the performance of their ceramic materials
426 by the addition of clays that are rich in pyroxenes.

427 The results showed that larger amounts of silver ions can be sorbed than silver
428 nanoparticles. However, the desorption of silver nanoparticles from the ceramic materials was
429 less than that of silver ions. Since it is known that silver is critical to the high performance of the
430 filter and that silver nanoparticles are desorbed to a lesser extent, they can be expected to have a
431 longer service life and to pose lower risks to the environment and human health.

432 Water chemistry is very important for preparing effective silver solutions during the
433 manufacturing process. Water quality does not matter as much for ionic silver applications, but
434 it is important when silver nanoparticles are used. The nanoparticles did not sorb well with the
435 divalent calcium solution, so excessively hard water may not be appropriate for use in preparing
436 nanoparticle solutions for use in CWFs.

437 In this study, the factor that had the most significant influence on the strength of CWFs
438 was the region of manufacturing, and this was likely due to differences in the clay mineralogy of
439 the source materials. Potentially, the factor that ranked second relative to its influence on the
440 strength of CWFs was the part of the filter that was tested. The factor that had the least influence
441 on the strength of CWFs was the loading direction. In fact, the highest strengths occurred when
442 the samples were loaded from the outside inward, suggesting that the pressing during the
443 manufacturing process did not induce significant anisotropy in the material.

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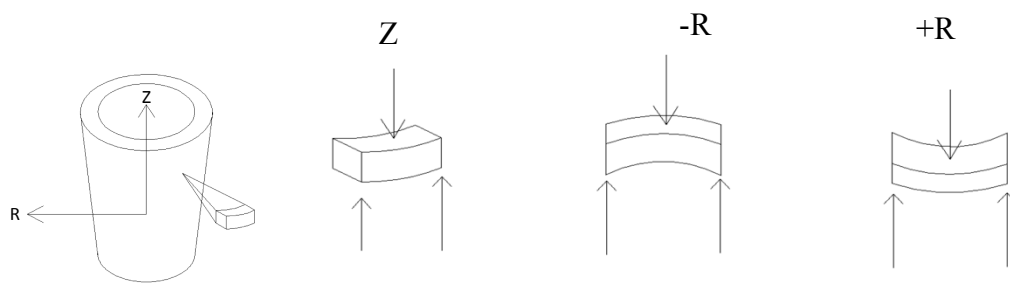
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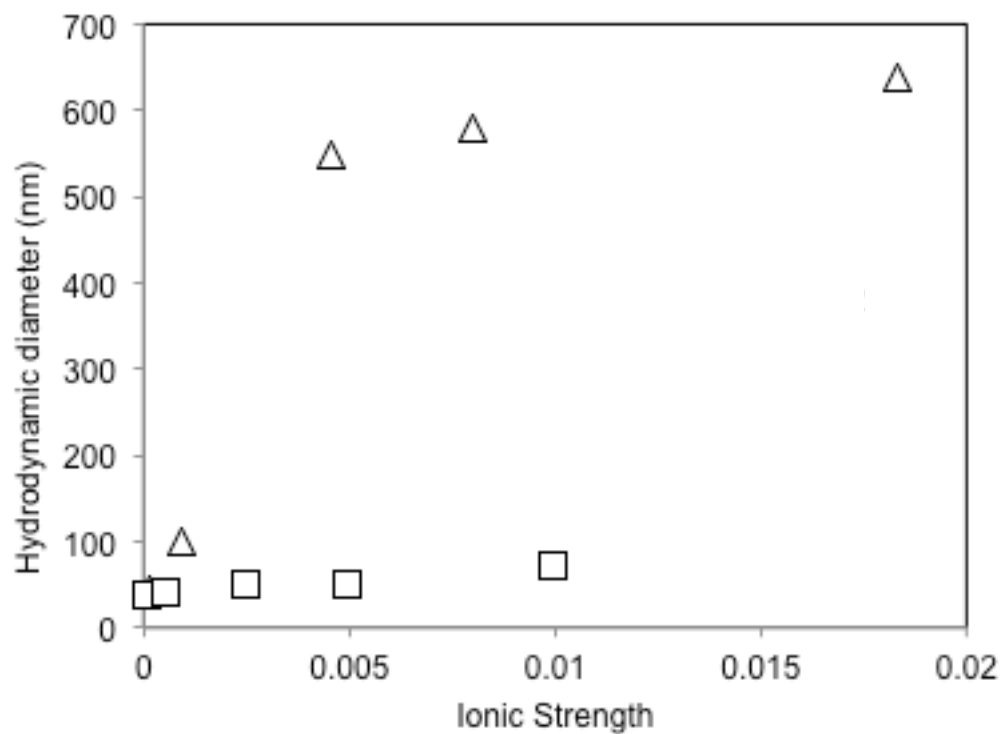


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Figure 1. Orientation of beam specimens that were cut from the sides of the CWFs.

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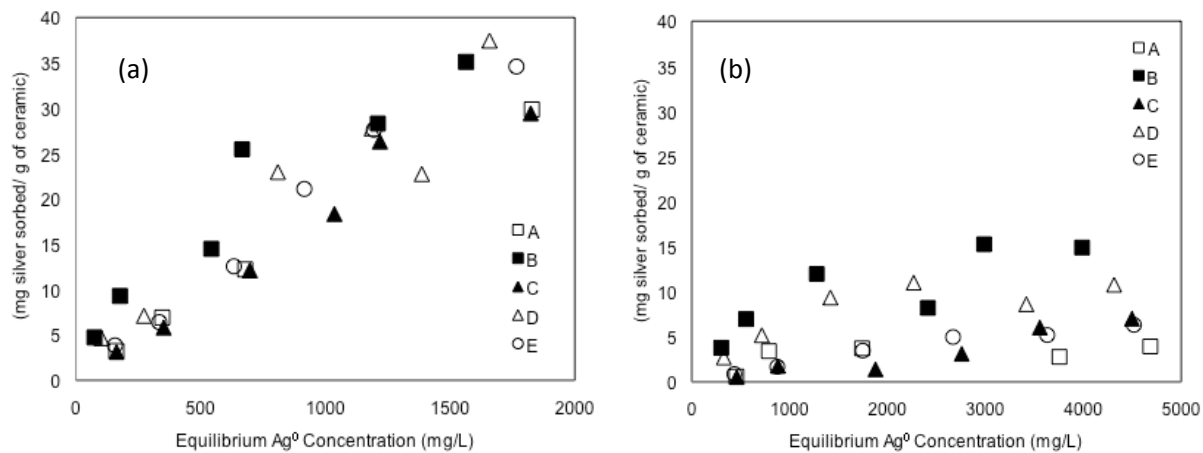


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525 **Figure 2. Evolution of the hydrodynamic diameter at increasing ionic strength of**
526 **monovalent (KNO₃; squares) and divalent (Ca(NO₃)₂; triangles) electrolytes solutions**

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530 **Figure 3. Silver nanoparticle sorption isotherms for ceramics (A) USA, (B) Guatemala, (C)**

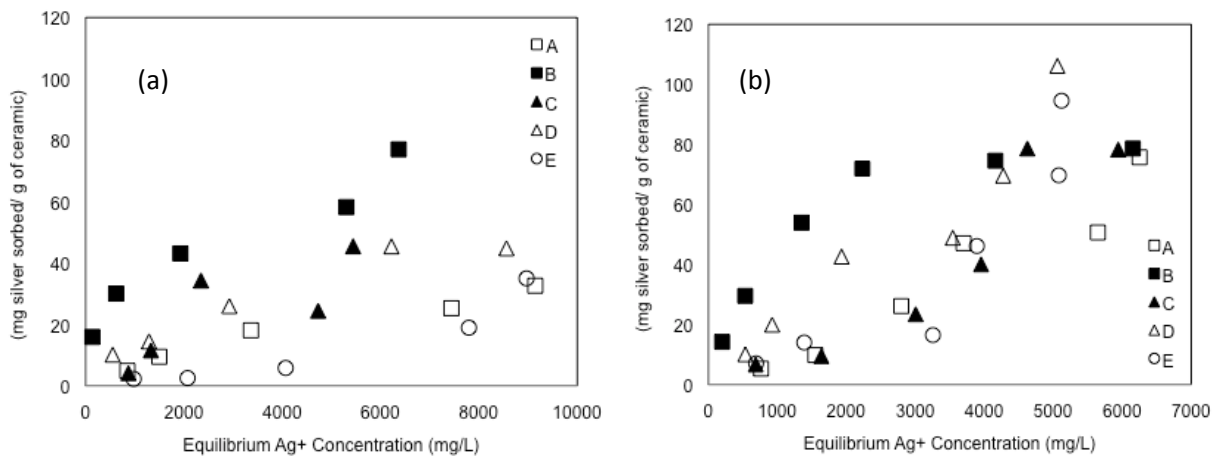
531 **Ghana, (D) Peru and (E) Nicaragua at the water chemistry conditions (a) KNO_3 , and (b)**

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$Ca(NO_3)_2$

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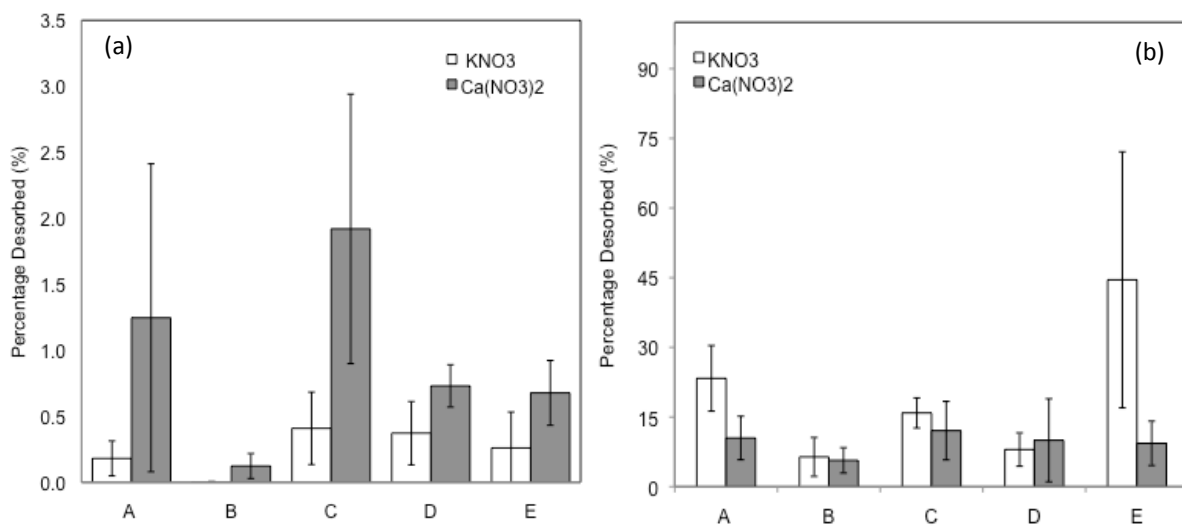
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536 **Figure 4. Silver ions sorption isotherms for ceramics (A) USA, (B) Guatemala, (C) Ghana,**

537 **(D) Peru and (E) Nicaragua at the water chemistry conditions (a) KNO₃, and (b) Ca(NO₃)₂**

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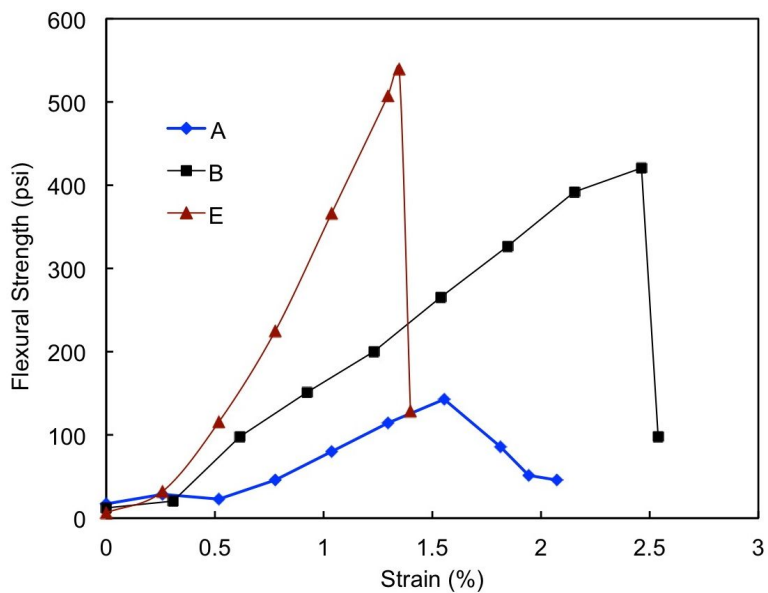
541 **Figure 5. (a) Percentage of silver nanoparticle desorption and (b) percentage of ionic silver**
542 **desorption at different water chemistry conditions for ceramics from (A) USA, (B)**
543 **Guatemala, (C) Ghana, (D) Peru and (E) Nicaragua**

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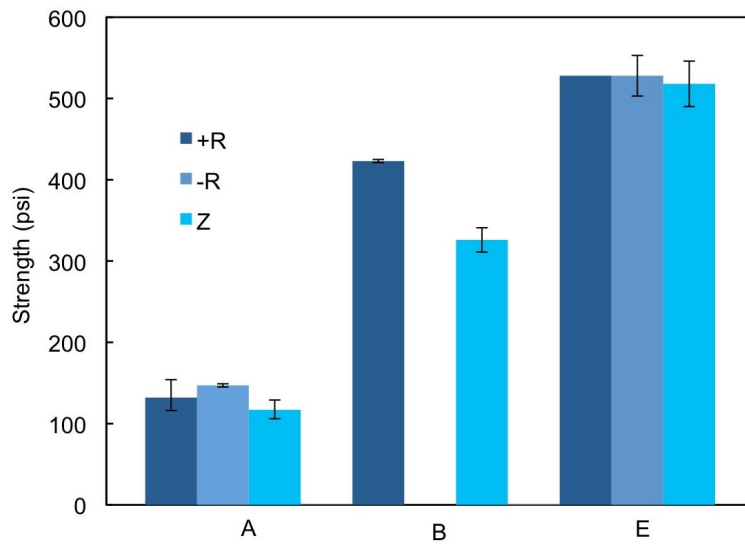
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Figure 6. Typical flexural test results from three CWF sources under the same loading orientation (+R direction). (A) USA, (B) Guatemala, and (E) Nicaragua

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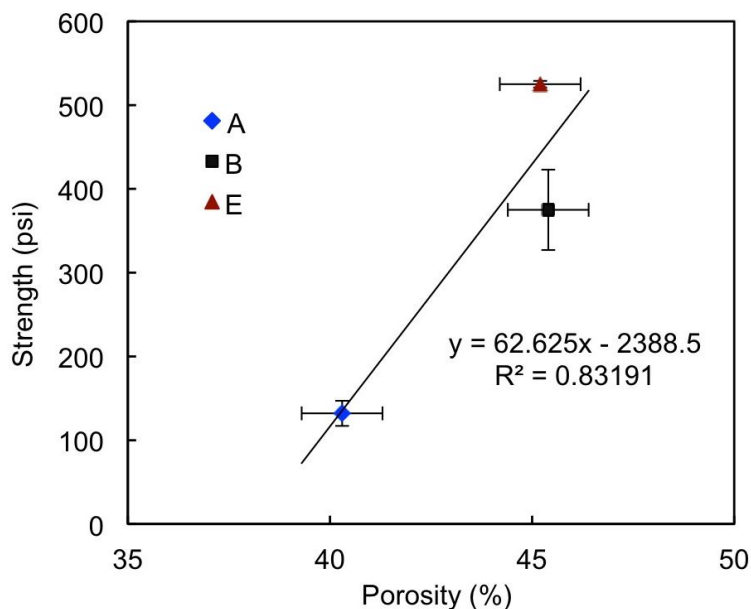
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Figure 7. Summary of flexural strength test results for three CWF sources. The error bars shown represent the minimum and maximum measured strength. (A) USA, (B) Guatemala, and (E) Nicaragua.

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562 **Figure 8. Correlation between flexural strength and porosity for the +R loading**
563 **direction for three CWF sources. The error bars shown represent the minimum and**
564 **maximum values. (A) USA, (B) Guatemala, and (E) Nicaragua**
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600 Table 1. Summary table of bulk powder XRD and XRF results. All samples were analyzed under
 601 identical conditions.

Sample provenance	Bulk XRD	Bulk XRF	Additional notes
USA	Quartz, minor 16Å smectite group clay	K, Ti, Cr	Illite suggested by minor peak at 3.49 Å (small peak area, irregular boundary).
Guatemala	Quartz, pyroxene (likely derived from arc volcanics), minor 16Å smectite group clay	Ca, Ti, Mn, Fe, Eu	Abundant volcanic ash from nearby convergent margin magmatism along the western boundary of Central and South America is likely the precursor to clay units utilized in this ceramic.
Ghana	Essentially all quartz, minor 16Å smectite group clay	K, Ti, Cr, Fe	Geologic units of this region of Northern Ghana include shales and sandstones of the Voltaian Group (Anani, 1999), leading to a quartz-rich source with clays derived likely from sedimentary formations.
Peru	Quartz, albite, possible illite, and minor 16Å smectite group clay	K, Ca, Ti, Fe, possible Sn	This clay source is also likely derived from volcanic ash.
Nicaragua	Quartz, albite, illite-group clay, minor 16Å smectite group clay, and pyroxene.	Ca, Ti, Cr, Mo, Fe, Mn, Eu, Pm	High background suggests poorly crystalline matrix. This clay source is likely derived from volcanic ash.

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Table 2. Fitting parameters for all the experiments

	Sample	Langmuir			Freundlich		
		Q_M	b_A	R^2	n	K	R^2
$Ag^0 - Ca(NO_3)_2$	A	13.8	0.4	0.65	1.791	0.039	0.78
	B	65.0	0.3	0.74	2.136	0.313	0.79
	C	4.9	0.8	0.47	0.966	0.001	0.87
	D	60.7	0.2	0.92	1.955	0.170	0.83
	F	10.0	1.8	0.81	1.165	0.005	0.98
$Ag^0 - KNO_3$	A	63.7	6.6	0.49	1.059	0.027	0.99
	B	90.0	0.6	0.82	1.548	0.305	0.97
	C	33.3	23.3	0.45	1.010	0.019	0.99
	D	62.2	1.0	0.57	1.346	0.135	0.96
	F	38.9	14.5	0.45	1.035	0.027	0.99
$Ag^+ - Ca(NO_3)_2$	A	74.8	1.7	0.56	0.785	0.001	0.97
	B	570.6	0.2	0.99	1.959	1.131	0.93
	C	39.1	0.2	0.43	0.799	0.001	0.91
	D	102.8	5.0	0.41	1.075	0.032	0.96
	F	40.1	0.3	0.32	0.863	0.003	0.84
$Ag^+ - KNO_3$	A	4.4	0.6	0.90	1.327	0.034	0.97
	B	11.4	0.8	0.94	2.606	2.416	0.98
	C	36.8	0.8	0.45	0.918	0.004	0.78
	D	143.1	0.5	0.94	1.688	0.228	0.98
	F	12.0	0.2	0.42	0.800	0.000	0.88

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