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Calcined Waste Eggshells Remove Sulfate in Non-Potable Concrete Mixing Water

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Abstract

The experimental and theoretical potential of using calcined waste eggshells (CWEs) to remove sulfate from sulfate-laden concrete mixing water was investigated in this work. Waste eggshells were first calcined at 800 ˚C and batch-reacted with sodium sulfate solutions. Laboratory experiments elucidated the effect of initial sulfate concentration, temperature of reaction, and CWE particle size on total sulfate removal. Experimental results indicate a maximum sulfate removal of 29.5 ± 2.2% via calcium sulfate mineral precipitation in laboratory batch reactions. To quantify maximum sulfate removal potential of CWEs, batch reactions were simulated using PHREEQC, a geochemical code. After validating the simulation approach with experimental data obtained herein, PHREEQC was used to investigate the maximum sulfate removed as a function of CWE addition (g/L). Results indicate that sulfate-laden waters (≤4,000 ppm) can be decreased to ≤3,000 ppm with CWE additions of ≥3 g/L in order to comply with ASTM C1602, the standard specification for maximum allowable sulfates in water intended for use in the production of hydraulic cement concrete.

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Introduction

Adequate water for concrete mixtures could become a scarce resource. Experts predict that half of the world's population will be living in water-stressed areas by 2025 ("Drinking Water Fact Sheet" 2017). In industrial applications, potable water is used for concrete mixing, while regions facing water scarcity are constrained instead to use surface waters or wastewaters (Su, Miao, and Liu 2002; Al-Jabri et al. 2011). The quality of mixing water affects both fresh- (Gholamreza Asadollahfardi et al. 2015; Ismail and Al-Hashmi 2011) and hardened-state (Chatveera and Lertwattanaruk 2009; Xuan et al. 2016; Ghrair et al. 2016; Barrera-Díaz et al. 2011) properties of concrete, and the presence of excess physical and chemical substances in non-potable water (e.g., suspended solids, chloride, sulfate) can subsequently compromise the long-term durability of concrete. For example, Asadollahfardi et al. found that wastewater decreased ~10% of compressive strength after rapid freeze-thaw durability testing compared to concrete mixtures using potable water (G. Asadollahfardi et al. 2016).

Watersheds affected by mining drainage or endemic geological features may exhibit surface waters with high levels of sulfate. Mining sites, even after closure, act as long-term sulfate pollutant sources, contaminating both groundwater and surface waters. In Germany, for instance, the Lausitz mining district is predicted to discharge ~11,000 tons of sulfate per year within the next 40 years to the Kleine Spree and Spree rivers (Graupner, Koch, and Prommer 2014). In 2008, the United States Geological Survey (USGS) reported a broad range of sulfate concentrations (from 100 to 8,000 ppm) within the Red River Valley in Taos County, New Mexico from both natural oxidation of pyrite-rich mineralized rock and waste-pile rocks from previous mining operations. Natural scar drainage and individual mine waste-pile rocks drainage have sulfate concentrations of approximately 2,000 ppm and >5,000 ppm, respectively (Nordstrom 2008). In some cases, waste-pile rock drainage was found to have sulfate concentrations up to 5,000 ppm, and scar drainage has been reported to reach sulfate concentrations of approximately 15,000 ppm (Robertson GeoConsultants 2000).

The presence of sulfates in concrete mixing water can result in damage or deterioration of concrete due to internal sulfate attack (Fu, Ding, and Beaudoin 1997; Crammond 2002). ASTM C1602 sets sulfate limits for concrete mixing water to a maximum of 3,000 ppm. Calcium- and barium-assisted precipitation are two common sulfate-reducing methods. Calcium-assisted precipitation of sulfate leverages dissolved calcium from lime (CaO) or, more explicitly, hydrated lime (i.e., portlandite) (($Ca(OH)_2$), that can react with available sulfate anions to precipitate calcium sulfate compounds. However, the solubility of the calcium sulfate precipitate is approximately 2,000 ppm, thus limiting precipitation to sulfate concentrations above 2,000 ppm (Bowell et al. 1998). In addition, this method requires the energy- and resource-intensity of mining of limestone, which may be a prohibiting factor in some water-stressed areas. To further reduce the concentration of sulfate, barium chloride salt may be used after lime treatment. However, the cost of this method is high, and the presence of chlorides has tangential consequences in the removal of sulfates for mixing water intended for steel-reinforced concrete applications (Bowell 2000).

Scope of Work

Given that removal of sulfate from sulfate-laden mixing water in water-stressed areas must be inexpensive and easy to implement, this work investigates the viability of calcium-assisted removal of sulfate anions using calcined waste eggshells (CWEs), which are naturally abundant in calcite ($CaCO_3$). While previous studies have investigated the use of CWEs, to remove other water contaminants from wastewater, such as cadmium and phosphate, (Köse and Kivanç 2011; Kuh and Kim 2000), to the authors' knowledge no other studies have investigated the use of CWEs as a primary calcium source for calcium-assisted sulfate removal. In addition to experimental batch reactions, a geochemical simulation modeling code (PHREEQC) was used in this study for experimental verification, validation, and prediction of sulfate removal to investigate the maximum sulfate removed as a function of CWE addition (g/L).

Materials and Methods

Materials

Waste eggshells were collected from a residential waste stream. Sodium sulfate (ACS reagent, ≥99%) was obtained from Sigma-Aldrich Millipore.

Experimental methods

Eggshell calcination

Eggshells were washed with tap water, and their inner membranes were removed. The shells were dried in a Quincy forced-air laboratory oven set to 100 ˚C for 24 hours. To isolate two particle sizes, the dried eggshells were ground and screened through No. 100 (particle size < 149 µm) and No. 325 (particle size < 44 µm) sieves. The waste eggshell powders were then calcined in a Hach Furnace Muffle 1300 set to 800 ˚C for one hour, as reported in (Köse and Kivanç 2011).

Batch Reactions

Sulfate removal was experimentally investigated as a function of (1) initial sulfate concentration, (2) temperature of reaction, and (3) particle size using batch reactions of sodium sulfate (Na_2SO_4) solutions dosed with calcined waste eggshells (CWE) at a constant weight ratio (Na_2SO_4:CWE = 2.73). Three sulfate concentrations were explored, namely high (13,440 ppm), medium (7,680 ppm), and low (1,920 ppm), which corresponded to CWE additions of 7.28g/L, 4.16 g/L, and 1.04 g/L, respectively. Batch reactions were covered and constantly stirred for 24 hours using a Scilogex analog 10-channel magnetic stir plate. After 24 hours, the precipitate was separated from the solution *via* vacuum filtration employing Q5 filter paper (Fisher Scientific, medium porosity and flow). The precipitate was collected and dried in a Quincy forced-air laboratory oven set to 45 ˚C for at least 24 hours. Two reaction temperatures were explored, namely unheated (22±4˚C) and heated (46±6˚C), by varying the temperature settings of the magnetic stir plate.

Statistical analysis of data

The statistical analysis software, Minitab 18.1, was used to analyze the significance of experimental results.

X-Ray Diffraction (XRD)

XRD was employed to determine mineralogy of CWEs and to verify precipitates from the sulfate removal experiments. Powders were prepared for analysis using a method previously published in (Eberl 2003).

Ion Chromatography (IC)

The initial and final concentration of total sulfate-containing molecules were measured on a Dionex 4500i ion chromatograph. Four National Institute of Standards and Technology (NIST) traceable standards were used for calibration. An AG14 guard column and AS14 column were used for separation of anions. Triplicates were used to calculate the concentration means, which were reported in parts per million (ppm) of total sulfate compounds.

Computational methods

PHREEQC (v.3.3.12.12704), a geochemical simulation code developed by the United States Geological Survey (USGS), was used to simulate CWE batch reactions in Na_2SO_4 solutions (Parkhurst, D.L., and Appelo, C.A.J. 2013). In the present study, equilibrium reactions and phase assemblages were defined to simulate Na_2SO_4 solutions at the three sulfate concentrations (simulation verification). Chemical thermodynamic data for the dissolution of primary and secondary minerals was obtained from the Minteq database (minteq.v4.dat). Values used in the simulation are presented in **Table 1**.

Thenardite was used as the model reagent to simulate Na_2SO_4. XRD was first used to identify the mineralogy of CWEs, which were composed of a ternary mixture of lime, calcite, and portlandite. During calibration, varying the composition of lime, calcite, and portlandite enabled approximation of CWE mineralogy and permitted simulation of batch reactions. Finally, the calibrated simulation was used to predict the maximum removable sulfate from sulfate-laden waters as a function of CWE addition (g/L).

Results and Discussion

CWE Calcination

The calcination process decarbonates calcite ($CaCO_3$) into lime (CaO) which, when hydrated, becomes portlandite ($Ca(OH)_2$). Mineralogy results, shown in **Figure 1**, confirm that calcite ($CaCO_3$) is the main mineral found in uncalcined eggshells. During calcination, calcite decarbonates, releasing carbon dioxide (CO_2), yielding lime (CaO) (Flamant et al. 1980):

$$CaCO_3 \leftrightarrow CaO + CO_2$$

Due to the presence of water in the environment, CaO can hydrate to form portlandite ($Ca(OH)_2$) (Serris et al. 2011):

$$CaO\ (s) + H_2O\ (g) \rightarrow Ca(OH)_2\ (s)$$

The results substantiate that the conversion of calcite to lime and portlandite is only partial due to the calcination process employed herein. As a result, CWEs achieved herein were mainly composed of portlandite and calcite, with traces of lime (**Figure 1**).

Effect of temperature and particle size on sulfate removal

At room temperature, 29.5% of sulfates can be removed by addition of CWEs (**Figure 2**). No significant difference in sulfate removal between medium and high initial sulfate concentrations was observed, as verified by an analysis of variance (ANOVA). For unheated solutions of medium and high initial sulfate concentrations, ANOVA yielded a p-value of 0.09. The p-value for heated solutions of these two initial sulfate concentrations was higher (0.41). Thus, results substantiate that, in both unheated and heated batch reactions, no significant differences in sulfate removal exist between both medium and high initial sulfate concentrations. At low initial sulfate concentrations, the sulfate concentration was below the solubility limit of gypsum (2070 ppm at 25C°) (Bock 1961), thereby preventing gypsum precipitation and prohibiting sulfate removal.

For all solutions with initial sulfate (high or medium), increased temperature resulted in decreased sulfate removal (**Figure 2**). As expected from Le Chatelier's principle, higher temperatures increased the supersaturation limit of calcium sulfate (gypsum) due to an increased equilibrium constant of gypsum precipitation. As observed in **Figure 2**, heated batch reactions (46 ± 6˚C) had, on average, decreased sulfate removal by approximately 53% as compared to unheated batch reactions (22 ˚C ± 4˚C). Heated batch reactions at low concentrations, however, neither increased nor decreased sulfate removal.

Contrary to expected increases in sulfate removal kinetics due to higher surface area, reduced CWE particle size does not affect sulfate removal (**Figure 2**). For example, in unheated batch reactions at medium initial sulfate concentrations, the mean sulfate removal for CWEs of particle size 149 μm (sieve #100) and 44 μm (sieve #250) was 29.63 ± 1.76 and 29.40 ± 2.91, respectively. These results are evidenced by the means and standard deviations shown in **Figure 2**. To verify this conclusion, an ANOVA was performed on the means of the sulfate removal percentages for each batch reaction with different temperatures and particle sizes. Particle size of CWE was verified to negligibly affect sulfate removal regardless of initial sodium sulfate concentration and batch reaction temperature (p-values of 0.45 and 0.89 for both groups of heated and unheated batch reactions, respectively). As a result, calcium sulfate precipitation was not affected by differences in particle sizes investigated herein.

Mineralogy of sulfate precipitates

Sulfate removal by CWE precipitates calcium sulfate compounds. These precipitates can contain remnants of unreacted portlandite at high initial sulfate concentrations. Particle size does not influence the type of precipitated minerals as observed in **Figure 3a,** and **Figure 3b**. Moreover, the reaction of sulfate-laden water with CWE results in the precipitation of gypsum ($CaSO_4$:$2H_2O$) and bassanite, a calcium sulfate hemihydrate, at both medium (**Figure 3c**) and high initial sulfate concentrations (**Figure 3a, Figure 3b**). While calcite (from the original, uncalcined eggshell composition) is present at both medium and high initial sulfate concentrations, portlandite (from the CWE) is only present in high initial sodium sulfate concentrations. Unreacted portlandite is expected at higher CWE additions, as the batch reactions cannot react all portlandite due to the solubility equilibrium limit of portlandite itself (1130 ppm at 25°C) (Miller and Witt 1928; Noyes and Chapin 1899).

Computational simulations of sulfate removal

Simulation verification

Initial sulfate solutions were simulated using PHREEQC, and the results show a 0.02% error compared to experiments, thus verifying the ability of PHREEQC to simulate initial sulfate concentrations. As explicated in the computational methods section, experimentally known quantities of Na_2SO_4 were used as inputs for the simulation at standard temperature and pressure. PHREEQC predicts the equilibrium dissolution of thenardite at three different concentrations. The error, which was calculated by comparing both experimental and simulation results (**Table 3**), is within 0.02% for all values, providing adequate verification for the code to simulate thenardite dissolution in water.

Simulation calibration

The approximate mineral composition of CWEs was determined to be 10% lime, 30% calcite, and 60% portlandite by utilizing a combination of (1) experimental data and (2) a statistical analysis of simulation data. This quantitative mineral composition agrees with the qualitative XRD information of CWEs (**Figure 1**).

Results from the ternary mixture design reveal that portlandite has a larger effect on sulfate removal and, as expected, calcite has little to no effect. Executing a response optimizer function at initially high sulfate levels, a global solution for CWE mineralogy was found to be: 34.35% lime, 0% calcite, and 65.65% portlandite. Thus, in order to fit both experimental (**Figure 1**) and simulation results, the mineral composition of CWEs was assumed to be calcite 30%, lime 10%, and 60% portlandite to retain values near the global solution. As seen in **Table 4**, the simulation results for the approximated mineralogy of CWEs are in good agreement with experimental results within their standard deviation, validating that PHREEQC is adequate to represent the studied system.

Effect of CWE addition on sulfate removal

To investigate the theoretical sulfate removal potential of CWEs, a computational experiment of multiple batch reaction simulations was performed, and the results are presented in **Figure 4**. Addition of CWEs is represented as grams of CWE added to liters of sulfate solution (g/L). **Figure 4** indicates that CWE additions above 7 g/L do not yield increased sulfate precipitation. Further validating the simulation results, experimental results are plotted in **Figure 4**. The experimental values are in good agreement with the simulation, which further validates the adequacy of the simulation to predict real case dissolution-precipitation scenarios.

CWE-assisted precipitation of sulfates is an effective method to reduce sulfates in concrete mixing water. In order for concrete mixing water to comply with the allowable sulfate limit set by ASTM C1602 (3000 ppm), an initial total sulfate concentration of approximately ≤4000 ppm can be successfully treated using CWEs. Further illustrating this point, **Figure 4** demonstrates that an initial sulfate concentration of 4000 ppm treated with a CWE addition of 7 g/L can comply with ASTM C1602 by reducing the sulfate concentration to acceptable limits.

Figure 4 can serve as a tool for CWE-assisted precipitation of sulfates and, in turn, permit the valorization of a ubiquitous household waste. The use of CWEs to remove sulfates has the potential to provide adequate concrete mixing water where adequate concrete mixing water is a scarce resource. As a result, this method has the transformative potential to improve the durability of future concrete infrastructure projects for specific industrial applications where mixing water may be compromised by high sulfate contents.

Conclusion

This study experimentally and theoretically investigated the viability of using of calcined waste eggshells (CWEs) to remove sulfates from sulfate-laden concrete mixing water. Calcination of waste eggshells produced portlandite, which was verified through simulation as the main factor affecting the removal of soluble sulfates. The addition of CWE to batch reactions with sodium sulfate precipitated calcium sulfate hydrate minerals, mainly gypsum. The maximum mean sulfate removal attained experimentally was 29.51% ± 2.16% in medium initial sulfate solutions (7,680 ppm). The addition of heat in batch reactions decreased sulfate removal up to 53%. In addition, increased surface area via reduction of CWE particle sizes neither improved nor hindered reactivity or ultimate sulfate removal. Simulation results predict that CWEs can be used to treat concrete mix water with up to 4,000 ppm of soluble sulfates in order to yield compliant concrete mixing water, as specified by ASTM C1602. These findings highlight an opportunity for valorization of a ubiquitous waste material in an application that contributes to the long-term durability of civil infrastructure in resource-limited environments.

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List of Figure Captions

Figure 1. XRD diffractogram of eggshells before (a) and after calcination (b). Mineral symbols are defined in table 2. Figure symbols represent the following minerals – C: Calcite, L: Lime, P: Portlandite, G: Gypsum, B: Bassanite, and O: Corundum.

Figure 2. Sulfate removal for heated (46 ± 6˚C) and unheated (room temperature) batch reactions with particle sizes of 149 µm (sieve #100) and 44 µm (sieve #325) exposed to low (1,920 ppm), medium (7,680 ppm), and high (13,440 ppm) initial sulfate concentration. No sulfate removal was observed at low initial sulfate concentrations.

Figure 3. Representative XRD diffractograms of precipitates at high initial sulfate concentration (13,440 ppm) using CWE particle sizes of (a) 149 µm (sieve #100), (b) 44 µm (sieve #325). Figure symbols represent the following minerals – C: Calcite, L: Lime, P: Portlandite, G: Gypsum, B: Bassanite, and, O: Corundum.

Figure 4. Effect of CWE addition in grams per liter (simulated as a ternary blend of portlandite ($Ca(OH)_2$), lime (CaO), and calcite ($CaCO_3$)) on final sulfate (SO_4) concentration when added to sulfate-laden solutions.

Experimental values correspond to the following initial sulfate concentrations: low (1,920 ppm), medium (7,680 ppm), and high (13,440 ppm).

List of Tables

Table 1. Chemical thermodynamic data used in geochemical simulation collected from the Minteq.v4. database (United States Environmental Protection Agency (U.S. EPA) 1991; Gustafsson 2011; Allison, Brown, and Novo-Gradac 1991), (Stumm and Morgan 1996).

	Dissolution Reaction	**log K**	**ΔH** *(kJ/mol)*
Primary Minerals			
Thenardite (Na_2SO_4)	$Na_2SO_4 \leftrightarrow 2Na^+ + SO_4^{-2}$	0.32	-9.12
Portlandite ($Ca(OH)_2$)	$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{+2} + 2H_2O$	22.80	-128.62
Lime (CaO)	$CaO + 2H^+ \leftrightarrow Ca^{+2} + H_2O$	32.70	-193.91
Calcite ($CaCO_3$)	$CaCO_3 \leftrightarrow Ca^{+2} + CO_3^{-2}$	-8.48	-8.00
Secondary Minerals			
Gypsum ($CaSO_4{:}2H_2O$)	$CaSO_4{:}2H_2O \leftrightarrow Ca^{+2} + SO_4^{-2} + 2H_2O$	-4.36	1.00
Anhydrite ($CaSO_4$)	$CaSO_4 \leftrightarrow Ca^{+2} + SO_4^{-2}$	-4.61	1.00
Mirabilite ($Na_2SO_4{:}10H_2O$)	$Na_2SO_4{:}10H_2O \leftrightarrow 2Na^+ + SO_4^{-2} + 10H_2O$	-1.11	79.44

Table 2. Summary of minerals found using XRD and corresponding symbols. Symbols correspond to peak identification.

Mineral name	Stoichiometry	Symbol	Unit geometry	Density (g/cm^3)	Reference
Calcite	$CaCO_3$	C	Hexagonal	2.71	00-005-0586
Lime	CaO	L	Cubic	3.346	00-037-1497
Portlandite	$Ca(OH)_2$	P	Hexagonal	2.243	00-044-1481
Gypsum	$CaSO_4 \cdot 2H_2O$	G	Monoclinic	2.32	00-033-0311
Bassanite	$CaSO_4 \cdot 0.5H_2O$	B	Monoclinic	2.69	00-041-0224
Corundum	Al_2O_3	O	-	-	00-010-0173

Table 3. Experimental and computational results of initial total dissolved sulfate. Initial sulfate concentrations: low (1,920 ppm), medium (7,680 ppm), and high (13,440 ppm).

	Low	**Medium**	**High**
Experimental (IC)	0.004999	0.019994	0.034990
Simulation (PHREEQC)	0.005	0.020	0.035

Table 4. Experimental and simulated results for the sulfate removal at standard temperature and pressure conditions. Initial sulfate concentrations: low (1,920 ppm), medium (7,680 ppm), and high (13,440 ppm).

	Low	**S.D.**	**Medium**	**S.D.**	**High**	**S.D.**
Experimental (IC)	0%	-	30%	2%	27%	2%
Simulation (PHREEQC)	0%	-	32%	-	29%	-