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Treatment of concrete wash wastewater from ready-mix concrete operations

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ABSTRACT

Wash wastewater generated from ready-mix concrete (RMC) drums poses major environmental problems due to its high alkalinity and elevated heavy metal contents that need to be removed prior to disposal. The present study aims at developing a technology that will be able to reduce chromium and strontium concentrations as well as effluent pH to acceptable disposal levels set by various environmental agencies. Representative samples of wash wastewaters from RMC trucks were prepared and different treatment technologies were evaluated for their efficiencies of removing chromium and strontium present in solution. Sample characterizations indicated that the alkaline wash wastewater contained elevated concentrations of chromium and strontium at levels of 2.59 and 12.26 mg/l, respectively. Treatment of wash wastewater with barium chloride lowered the chromium to non-detectable limits. Whilst treatment with disodium hydrogen phosphate lowered the strontium to less than 0.063 mg/l, it is then hypothesized that sequence treatment of barium chloride, disodium hydrogen phosphate, and carbon dioxide bubbling will result in an effluent solution with acceptable disposal characteristics that satisfy regulatory bodies.

Keywords: Wash wastewater; Ready-mix concrete; Chromium; Strontium; Chemical precipitation; Ion speciation; Saturation index; Mineral formation

1. Introduction

Construction activities in the United Arab Emirates have been going at extremely high rates for the last decades resulting in several huge ready-mix concrete (RMC) batch plants in the country. A recent survey reported that 58 major RMC batching plants are in operation posing serious environmental concerns associated with polluted wastewater generated from washing the mixer drums, after dumping the concrete on sites [1]. According to the water quality act, truck wash wastewater is a hazardous substance because it contains caustic soda and potash and its disposal is regulated by the Environmental Agency. In addition, a high pH makes truck wash wastewater hazardous under US Environmental Protection Agency's (EPA) definition of corrosivity.

The quality of RMC wastewater is derived from the source of the water itself. Wash wastewater discharge from truck wash contains cementitious materials and

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chemical admixture residue. Due to the high content of dissolved limestone solids, the wash wastewater is caustic and has a high pH value ranging from 11 to 12 [2,3]. In general, the wastewater contains dissolved solids which include: sulfates and hydroxides from cement, chlorides from the use of calcium chloride as an admixture, and small quantities of other chemicals associated with hydration of Portland cement and derivatives from chemical admixtures [2,3].

Presence of heavy metals in RMC wastewater at high levels could threaten the structural integrity of roads, buildings, and sidewalks. It can also contaminate the nearby waterways, soil, and vegetation [4]. Of importance is the presence of high levels of chromium and strontium in RMC wastewater. Chromium is a toxic metal of widespread use. The presence of trivalent and hexavalent chromium in the environment is the cause of many well-documented toxic effects such as nausea, skin ulcerations, and lung cancer as stated [5-7]. Chromium is included in the US EPA list of priority pollutants [8]. International Agency for Research on Cancer has classified chromium (VI) in Group 1 (carcinogenic to humans list) and chromium (III) in Group 3. According to US EPA, the maximum allowable concentration in drinking water for chromium is 0.1 mg/l. The World Health Organization international standards for drinking water recommended a maximum allowable concentration of 0.05 mg/l for chromium [9].

Problems with bone growth may occur in children eating food or drinking water with high levels of strontium. The US EPA recommends that drinking water levels of stable strontium should not exceed 4 mg/l [10,11]. Typically, the amount of strontium that has been measured in drinking water in different parts of the US by EPA is less than 1 mg/l [12].

1.1. RMC wastewater management practices

There are many ways of handling waste products generated from RMC plants. Reclaimed aggregates have already been quite extensively used in many countries for concrete batching purposes [13,14]. The common practices include:

- (1) Using concrete wash water pits or settling ponds at job sites or RMC plants for retaining disposed washout dumped directly from mixer trucks, of which the cementitious slurry is increasingly expensive to dispose off [13].
- (2) Using a series of settling ponds to recover washout that is relatively clean and free from solids for washing the inside of concrete truck mixer drums.

- (3) Using CO₂ to neutralize alkaline cement-based wastewater (pH about 12) for reuse or for discharging into public sewers [15].
- (4) Using mechanical reclaimer units to recycle or reuse cement-based wastewater.
- (5) Using chemical stabilizing admixture systems or agents to temporarily stop the cement hydration process so that the wash water can be reused for making concrete [16].

The preceding methods are either too costly to implement or require huge land space to be feasible.

1.2. RMC wastewater management practices in Dubai Emirate

In the Emirate of Dubai, United Arab Emirates, Dubai Municipality enforces all batching plants to have chromium reduction treatment facility. The usual treatment practice is described as follow:

- (a) wastewater flows through a three chambered sedimentation tank connected in series;
- (b) wastewater from the third sedimentation tank is pumped to a separate tank wherein dosing of ferrous sulfate (FeSO₄) and sulfuric acid (H₂SO₄) is applied. Ferrous sulfate is used to precipitate chromium, wherein it settles to the tank's bottom. Whilst, H₂SO₄ is used to lower wastewater pH to 3 since pH of untreated wastewater is usually 11–12;
- (c) wastewater is then pumped to another chamber and caustic soda (sodium hydroxide) dosing is added to bring pH within 7.5–8 from a level of 3 in the previous chamber;
- (d) wastewater is then pumped to a third chamber wherein a low speed motor is provided to further mix the wastewater; and
- (e) treated wastewater is then pumped to a separate tank wherein it is used for the same washing purpose.

Based on an overall assessment of the existing data from Dubai Municipality, no requirements for strontium removal from RMC wash wastewater. As such, this study seeks to determine suitable treatment method for concrete wash wastewater capable of producing water that can be safely recycled, reused or disposed off in water bodies without any harmful effects to humans and the environment.

2. Materials and methods

A survey of 58 RMC batching plants was conducted by Dubai Municipality in May 2006. The preliminary information about the plants and sources of cement, cement chemical admixtures, and aggregates used in the plants were collected from the survey. Representative cement, cement chemical admixtures, and aggregate samples were collected and analyzed for heavy metals including Zn, Ni, Cu, Cd, Pb, Cr, and Sr by flame atomic absorption spectrometer (FAAS). The results reveal a varying; yet high, concentration of chromium (Cr) in all analyzed cement samples. The National Cement Company (Dubai) and Admixture Conplast SP495 were found to have maximum concentration of chromium and strontium. Therefore, they were selected to prepare the critical RMC wash water sample considered in this study. Evaluating different treatment methods for the generated wash water implied working on a critical sample with ingredients producing the highest possible levels of chromium and strontium as detailed below.

2.1. Material

To design an RMC mix that leads to high levels of pollutants found in the analyzed concrete ingredients (mainly chromium and strontium), the mix should have low water/cement ratio to increase the cement and the additives as well as to increase the strength and durability of concrete. As reported by [17], the expected concrete slump is 0–10 mm and concrete strength is 60–70 MPa. The composition of the prepared mix is given in Table 1.

2.2. Sample preparation

The proposed mix design materials (Table 1) were delivered to the RMC batch plant where the selected components were blended in the rotating truck's mixer drum until delivery to the laboratory site at the University laboratory. Before the unloading, the driver washed down the concrete truck chute by water. The poured concrete was used in paving a parking lot near the laboratory. Since the truck concrete load was 2.30 m³, a volume of 45 l of tab water was poured into

Table 1 Composition of the critical RMC (1.0 m³)

Ingredients	Typical composition
Ordinary Portland cement	370 kg
Fine aggregate (sand & dune sand)	718 kg
Coarse aggregate (20 mm)	968 kg
Coarse aggregate (10 mm)	408 kg
Water	151 I
Cement chemical admixtures	11.1 kg
Water/cement ratio	0.41

the truck drum after unloading. The truck drum was agitated for 20 min to ensure complete mixing of the added fresh water with the residue concrete into truck drum. The wash wastewater from the truck drum was then discharged into large top open container. Prior to laboratory analyses, the RMC wash wastewater sample was kept and stored in two other large plastic containers (25 1 each) with sealed lids to prevent sample contamination.

2.3. Analytical methods

The presence of heavy metals such as Zn, Ni, Cu, Cd, Pb, Cr, and Sr were examined in the untreated RMC wash wastewater samples using flame atomic absorption spectrometer equipment (FAAS). The equipment used was Varian Spectra AA880 with double-beam spectrometer, spectral response 190–900 nm, fast response deuterium background corrector, rotating 8—lamp turret, and two burners both for air-acetylene and nitrous oxide-acetylene flame. The FAAS was calibrated before each set of measurements using the procedure specified in the manufacturer's manual. Quality control for FAAS analysis consisted of analysis of check samples and duplicates were performed to identify the precision and accuracy of FAAS results.

Ion chromatography was used to analyze major anions such as chloride, and sulfate in the wash-water sample. The equipment used for anion analyses was DIONEX DX500 modular chromatography system with conductivity, electrochemical, and absorbance detectors. Common anions are separated using an IonPac AS4A column. The ion chromatography was calibrated using calibration standards before each set of measurements using the procedure specified in the manufacturer's manual. A four point calibration was performed and an independent check quality control sample was analyzed every five samples to identify the precision and accuracy of the ion chromatography results.

Parameters such as total dissolved solids, total suspended solids, color, and pH were also measured. A number of screening tests were carried out in order to identify an eco-friendly and economically effective treatments of heavy metals-contaminated wash wastewater. The results were obtained upon conducting triplicates in each test and the average was taken and reported in this study with 1% coefficient of variation.

2.4. Sample characterization

Concentrations of various metals, heavy metals, and anions present in concrete wash wastewater sample are shown in Table 2. Of interest are the typical

Characteristics of prepared wash wastewater sample							
Concentrations (mg/l)							
Heavy metals (mg/l)	Zn 0.026	Ni 0.046	Cu 0.024	Cd 0.041	Pb 0.604	Cr 2.591	Sr 12.255
Metal cations (mg/l)	Al 0.2900	Ba 0.2229	Ca 772.58	Fe 0.009	K 473.65	Na 488.07	Mg 0.004
Anions (mg/l)	$\frac{\mathrm{SO}_4^-}{685}$	Cl ⁻ 88	HCO_3^-	CO ₃ 90	OH [−] 650		
Total suspended solids (1	ng/l)				3		
Total dissolved solids (mg/l)					5 <i>,</i> 890		
Total hardness (mg/l)					1,150		

Table 2 Characteristics of prepared wash wastewater sample

concentrations of chromium and strontium present in the wastewater, which are very high and measuring 2.591 and 12.255 mg/l, respectively. The pH was found to be 13.05. Table 2 also presents the levels of solids and hardness of the wastewater. It is worth mentioning that the raw concrete wash wastewater sample before settling was highly turbid while, after settlement, the color of the mixtures was yellowish.

2.5. Treatment methods

2.5.1. Dubai treatment method

An initial experiment using chemical precipitation process, as per the requirement of Dubai Municipality regulations, was conducted. Three chemicals; sulfuric acid (H₂SO₄), ferrous sulfate (FeSO₄), and sodium hydroxide (NaOH) were used for the removal of heavy metals from the wastewater sample. Fresh wash wastewater sample of 100 ml was transferred into clean glass bottle (250 ml with screw cap). About 0.1 g of ferrous sulfate (FeSO₄) and about three drops of sulfuric acid (H₂SO₄) were added to the bottle. The solution was mixed vigorously, and then 0.3 g of the sodium hydroxide (NaOH) was added. The liquid was kept on the shaker at $(25 \pm 1^{\circ}C)$ for 2 h. The solution was filtered through Whitman grade no 42 filter paper. Finally, Cr, and Sr concentrations were measured. The results shown in Table 3 indicate an excellent reduction of chromium using a mixture of several chemicals, but it was not effective for strontium removal.

2.5.2. Alternative treatment methods

Chemical precipitation operation is known to remove heavy metals from water [18]. In this study, the applicability of chemical compounds such as calcium carbonate (CaCO₃), calcium hydroxide Ca(OH)₂, calcium chloride (CaCl₂), calcium sulfate (CaSO₄), barium chloride (BaCl₂), sodium carbonate (Na₂CO₃), disodium hydrogen phosphate (Na₂HPO₄), and tetrasodium di-phosphate Na₄(PO₄)₂ in removing chromium and strontium were evaluated. Concentrations of chromium and strontium in the clarified solution were analyzed and the results are listed in Table 4. The data recorded indicate that the barium chloride is more efficient in removal of chromium metal in substantial amounts from the concrete wash wastewater. For strontium, the maximum removal efficiencies in these experiments were obtained with disodium hydrogen phosphate (Na₂HPO₄) showing 99.48% efficiency in strontium precipitation. So, disodium hydrogen phosphate (Na₂HPO₄) was selected for further strontium treatment and barium chloride (BaCl₂) was selected for chromium treatment.

The removal of chromium and strontium from RMC wash wastewater using barium chloride and disodium hydrogen phosphate was investigated under different experimental conditions such as the effects of pH and the weights of barium chloride and disodium hydrogen phosphate. A new set of experiments were conducted in order to optimize the treatment conditions. Weights of 0.05, 0.10, 0.20, 0.30, 0.40, and

Table 3

Dubai treatment method for ready-mix wash wastewater

Sample identification	Sr (mg/l)	Sr removal (%)	Cr (mg/l)	Cr removal (%)
Untreated wash wastewater (feed) Mixture of chemicals (3 drops of H ₂ SO ₄ , 0.1 g of FeSO ₄ , and 0.3 g of NaOH)	12.255 9.677	_ 21.04	2.094 0.00	- 100.00

0.50 g from each chemical compound were tested with a sample volume of 100 ml. The mixing time for all tests was set at 120 min. Also, the weight of precipitates was reported.

2.6. Thermodynamic modeling

In this study, the chemical equilibrium model (MINTEQ) was used to calculate metal speciation, solubility equilibrium, and sorption for each treatment process at different input concentrations. The model combines state-of-the-art descriptions of sorption and complexation reactions.

3. Results and discussion

3.1. Barium chloride treatment

Fig. 1 shows the effect of barium chloride on the removal efficiency of strontium and chromium. More than 95% of chromium was removed with the addition of 2 g/l of BaCl₂ while 100% was achieved with the addition of 5 g/l. Strontium removal efficiency of 65% was achieved with the addition of 2 g/l of BaCl₂. However, increased loading of BaCl₂ resulted in appreciable decrease of strontium removal. Fig. 2 shows the increase of the amount of precipitates as BaCl₂ increases, and Fig. 3 shows almost constant pH as BaCl₂ increases.

Results obtained from the modeling exercise can be highlighted in view of pH variations, ionic strength, ionic speciation, and minerals formation. Fig. 3 shows the calculated pH with BaCl₂ which is consistent with measured values. The ionic strength increases as BaCl₂ increases, as shown in Fig. 2.

In view of ionic speciation, we will highlight only those related to chromium and strontium to be able to understand the experimental removal efficiency shown in Fig. 1. Table 5 indicates that chromium in solution exists in various forms such as $Cr(OH)_3$ (aq), $Cr(OH)_4^-$, CrO_4^{2-} , $NaCrO_4^-$, $KCrO_4^-$, and $CaCrO_4(aq)$ which will complex with various metals and heavy metals to form different types of minerals in aqueous and precipitated phases. Minerals remained in the aqueous form are $CaCrO_4(s)$, Cr(VI)-ettringite, $CrCl_3(s)$, $CrO_3(s)$, $Cu(OH)_2(s)$, $CuCO_3(s)$, $CuCrO_4(s)$, $K_2Cr_2O_7(s)$, $K_2CrO_4(s)$, $Na_2Cr_2O_7(s)$, $Na_2CrO_4(s)$, $PbCrO_4(s)$. Whilst, those in the precipitated forms are $Cr(OH)_3$ (am), Cr_2O_3 (c), $FeCr_2O_4(s)$, $MgCr_2O_4(s)$. These precipitated minerals contributed to the high removal efficiency of chromium as shown in Fig. 1.

Table 5 also indicates that strontium in solution exists in various forms such as Sr^{2+} , $SrOH^+$, $SrCl^+$, $SrSO_4(aq)$, and. $SrCO_3(aq)$ which will complex with various metals and heavy metals to form different types of minerals in aqueous and precipitated phases. SrCrO4(s) is the only formed aqueous solution mineral and remained in aqueous solution while, strontianite mineral is precipitated. Strontianite formation decreases with increasing $BaCl_2$ indicating the poor effect of $BaCl_2$ on the removal efficiency of strontium.

Fig. 4 shows all precipitated minerals as function of BaCl₂ concentration. The figure indicates that saturation indices of barite, CrOH₃(am), Cr₂O₃(c), FeCr₂O₄(s), Ni(OH)₂ (am), Pb(OH)₂(s), and witherite minerals increased with BaCl₂ increase while, saturation indices of aragonite, CaCO₃xH₂O, calcite, ettringite, MgCr₂O₄(s), portlandite, strontianite, and valerite decreased with the addition of BaCl₂.

3.2. Disodium hydrogen phosphate treatment

Fig. 5 shows the percentage removal of strontium and chromium for different dosages of disodium hydrogen phosphate 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 g/l. It is sufficient to reduce strontium concentrations in the wash wastewater sample to 0.063 mg/l using a dosage of 5.0 g/l of Na₂HPO₄. Fig. 6 shows the

Table 4

Percentage removal of Cr and Sr using alternative chemicals reagents

Sample identification	Sr (mg/l)	Sr removal (%)	Cr (mg/l)	Cr removal (%)
Untreated wash water (feed)	12.208	_	2.042	_
Calcium carbonate (CaCO ₃)	12.200	0.07	1.957	4.16
Calcium hydroxide $Ca(OH)_2$	12.029	1.47	1.936	5.19
Calcium chloride (CaCl ₂)	11.878	2.70	1.900	6.95
Calcium sulfate (CaSO ₄)	12.044	1.34	1.921	5.93
Barium chloride $(BaCl_2)$	7.787	36.21	0.00	100.00
Sodium carbonate (Na_2CO_3)	0.146	98.80	1.942	4.90
Disodium hydrogen phosphate (Na ₂ HPO ₄)	0.063	99.48	1.884	7.74
Tetrasodium diphosphate $Na_4(PO_4)_2$	0.973	92.03	1.858	9.01

		Concentra	tion (mg/l)					
Speciation		50	500	1,000	2,000	3,000	4,000	5,000
Cr(OH	$(1)_{2}^{+}$							
	Cr(OH) ₃ (aq)	5.557	5.765	5.764	5.764	5.763	5.761	5.76
	$Cr(OH)_{4}^{-}$	94.443	94.443	94.235	94.236	94.237	94.237	94.24
CrO_4^{2-}	() I							
1	CrO_4^{2-}	46.684	47.314	48.158	49.712	51.107	52.36	53.486
	NaCrO₄	1.879	1.863	1.854	1.838	1.824	1.811	1.799
	KCrO ₄	0.79	0.784	0.781	0.774	0.768	0.763	0.758
	$CaCrO_4(aq)$	50.647	50.038	49.207	47.676	46.301	45.066	43.956
Sr^{2+}								
	Sr^{2+}	76.083	76.96	77.56	78.554	79.333	79.948	80.436
	$SrOH^+$	9.773	9.288	9.144	8.876	8.636	8.421	8.228
	$SrCl^+$	0.043	0.333	0.544	0.95	1.336	1.706	2.062
	$SrSO_4(aq)$	11.353	10.8	10.253	9.327	8.573	7.948	7.422
	$SrCO_3(aq)$	2.746	2.618	2.499	2.293	2.122	1.977	1.852

Table 5 Variations of ionic speciation with BaCl₂ dosage

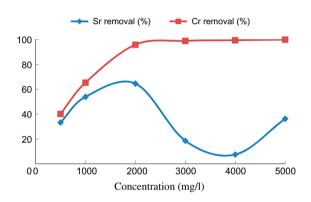


Fig. 1. Effect of $BaCl_2$ dosage on removal efficiency of strontium and chromium.

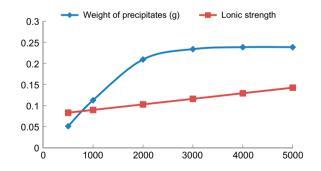


Fig. 2. Effect of $BaCl_2$ dosage on weight of precipitates and ionic strength of wash wastewater.

increase of the amount of precipitates as Na_2HPO_4 increases and Fig. 7 shows almost constant pH as Na_2HPO_4 increases. The constant pH values are consistent with the fact that pH of solutions made of a weak acid (mono potassium salt KH₂PO₄) and its salt (sodium salt, Na₂HPO₄) depends on the ratio of salt concentration to acid concentration. These salts ionize in solution to establish equilibrium $[H_2PO_4^2 \leftrightarrow H^+ + HPO_4^2]$.

The results shown in Fig. 8 are calculated by Minteq based on total phosphorus. The basic components of total phosphorous are H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} anions with different concentrations depending on solution pH. The results indicate that:

- (a) at pH greater than 12, HPO_4^{2-} , and PO_4^{3-} are present with $PO_4^{3-} > HPO_4^{2-}$;
- (b) at pH less than 10.61 and greater than 8.57, $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} are present in the following decreasing order $HPO_4^{2-} > PO_4^{3-} > H_2PO_4^-$; and
- (c) at pH7.27, H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3-} are present with the following decreasing order $HPO_4^{2--} > PO_4^{3-} > H_2PO_4^- > H_3PO_4$.

These results are consistent with Nakamoto [19] and Tejedor-Tejedor and Anderson [20] who reported that HPO_4^{2-} anion is predominant at pH 9 and also with Stumm and Morgan [21] who reported that $H_2PO_4^{-}$ anion is the predominant solution phosphate species at pH 6.

Table 6 shows the complex forms of various metal and heavy metal ions with PO_4^{3-} , HPO_4^2 , and $H_2PO_4^-$. Strontium forms $SrHPO_4$ (aq) and $SrH_2PO_4^+$ complex forms while, chromium complexes to form $CrHPO_4^+$.

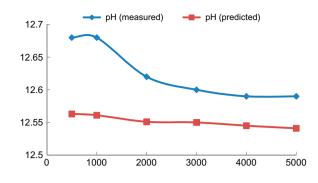


Fig. 3. Effect of BaCl₂ dosage on pH of wash wastewater.

Table 7 shows that Ba, Ca, Mg, and Sr formed solid minerals with HPO_4^{2-} in the forms of $BaHPO_4(s)$, $Ca_4H(PO_4)_3:3H_2O(s)$, $CaHPO_4(s)$, $CaHPO_4:2H_2O(s)$, MgHPO₄:3H₂O(s), and SrHPO₄(s). Some of these minerals reached saturation and precipitated while the others remained in suspended form. Similarly, various metal and heavy metal ions formed solid minerals with PO_4^{3-} such as $Ca_3(PO_4)_2$ (am1), $Ca_3(PO_4)_2$ (am2), Ca₃(PO₄)₂ (beta), chloropyromorphite, Cu₃(PO₄)₂(s), $Cu_3(PO_4)_2:3H_2O(s),$ hinsdalite, hydroxyapatite, hydroxylpyromorphite, $Mg_{3}(PO_{4})_{2}(s),$ $Ni_3(PO_4)_2(s)$, Pb₃(PO₄)₂(s), plumbgummite, tsumebite, vivianite, and $Zn_3(PO_4)_2$:4H₂O(s). Once again some of these reached saturation and precipitated while the others remained in suspended form. Precipitated minerals are shown in Fig. 9. The results indicate the formation of the following minerals aragonite, barite, brucite, Ca₃(PO₄)₂ (am1), Ca₃(PO₄)₂ (am2), CaCO₃xH₂O(s), calcite, Cr (OH)₃(am), $Cr_2O_3(c)$, ettringite, hydroxyapatite, $MgCr_2O_4(s)$, $Ni(OH)_2(c)$, $Pb(OH)_2(s),$ portlandite,

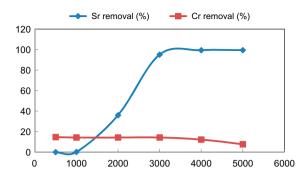


Fig. 5. Effect of Na_2HPO_4 dosage on removal efficiency of strontium and chromium.

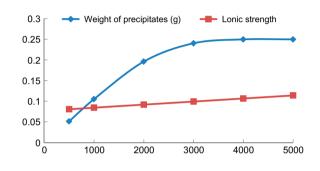


Fig. 6. Effect of Na_2HPO_4 dosage on weight of precipitates and ionic strength of wash wastewater.

strontianite, and vaterite. The high increase of new minerals due to increase of Na_2HPO_4 dosage has resulted in overall decrease in concentration of metal and heavy metals in the supernatant solution leading to high removal efficiency.

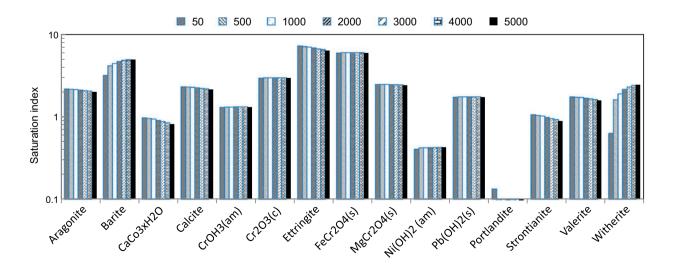


Fig. 4. Effect of BaCl₂ dosage on type of precipitated minerals.

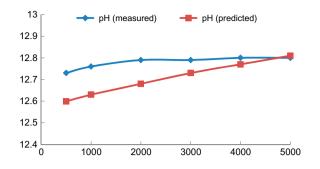


Fig. 7. Effect of Na₂HPO₄ dosage on pH of wash wastewater.

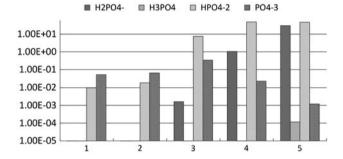


Fig. 8. Percent distribution of phosphorus anions with pH. Series 1 for pH 12.6; series 2 for pH 12.43; Series 3 for pH 10.61; Series 4 for pH 8.57; and Series 5 for pH 7.27.

3.3. Mixing time, sequence of treatment, and pH conditioning

The effect of mixing time on removal efficiency of chromium and strontium was studied by varying the

With HPO ₄ complexes	With PO_4^{3-} complexes
With HPO ₄ complexes BaHPO ₄ (s) Ca4H(PO ₄)3:3H ₂ O(s) CaHPO ₄ (s) CaHPO ₄ :2H ₂ O(s) MgHPO ₄ :3H ₂ O(s) SrHPO ₄ (s)	With PO_4^{g} complexes $Ca_3(PO_4)_2$ (am1) $Ca_3(PO_4)_2$ (am2) $Ca_3(PO_4)_2$ (beta)Chloropyromorphite $Cu_3(PO_4)_2(s)$ $Cu_3(PO_4)_2(s)$ HinsdaliteHydroxyapatiteHydroxylpyromorphite $Mg_3(PO_4)_2(s)$ Ni $_3(PO_4)_2(s)$ Pb $_3(PO_4)_2(s)$ PlumbgummiteTsumebiteVivianite $Zn_3(PO_4)_2(s)$

mixing period from 15 to 120 min while, keeping the doses of $BaCl_2$ at 5.0 g/l and Na_2HPO_4 at 3.0 g/l as constants. The results of the analyses are shown in Table 8. Quantitative removals of most of the Cr and Sr were obtained within a very short time (about 15 min). The precipitation of chromium and strontium did not change significantly with an increase in mixing time.

Table 6Complexation of metal and heavy metal ions with phosphate anions

Complexation with HPO ₄		Complexation wit	th H ₂ PO ₄	Complexation with PO_4		
Compound	Conc. (mole/l)	Compound	Conc. (mole/l)	Compound	Conc. (mole/l)	
$\begin{array}{c} \text{AlHPO}_4^+ \\ \text{BaHPO}_4 (aq) \\ \text{CaHPO}_4 (aq) \\ \text{CrHPO}_4^+ \\ \text{CuHPO}_4 (aq) \\ \text{FeHPO}_4 (aq) \\ \text{FeHPO}_4 (aq) \\ \text{HPO}_4-2 \\ \text{K2HPO}_4 (aq) \\ \text{KHPO}_4^- \\ \text{MgHPO}_4 (aq) \\ \text{Na}_2\text{HPO}_4 (aq) \\ \text{NaHPO}_4^- \\ \text{NiHPO}_4 (aq) \\ \text{PbHPO}_4 (aq) \\ \text{SrHPO}_4 (aq) \\ \text{ZnHPO}_4 (aq) \\ \end{array}$	4.5387E-37 1.2622E-15 2.8352E-11 1.4746E-35 4.8959E-26 2.975E-22 4.7071E-11 1.5956E-14 1.4112E-12 4.8568E-17 3.0378E-13 1.1733E-11 3.2501E-23 2.1258E-24 1.4067E-13 2.9488E-25	$\begin{array}{c} CaH_2PO_4^+\\ FeH_2PO_4^-\\ H_2PO_4^-\\ KH_2PO_4 (aq)\\ NaH_2PO_4 (aq)\\ NiH_2PO_4^+\\ PbH_2PO_4^+\\ SrH_2PO_4^+\\ SrH_2PO_4^+ \end{array}$	4.5113E-18 1.2168E-28 5.3375E-17 6.8497E-19 3.6769E-18 9.8998E-31 1.7348E-31 1.3241E-20	$\begin{array}{c} CaPO_4^-\\ MgPO_4^-\\ Na_2PO_4^-\\ NaPO_4^{-2}\\ PO_4^{-3} \end{array}$	6.4492E-07 1.2511E-14 4.8359E-11 1.577E-10 4.6135E-10	

Table 7

Mineralization

Mineralization of metal and heavy metal compounds with phosphate anions

To investigate the effect of the order of addition of these two chemicals on the chromium and strontium removals, the following two sequences were tested:

- first 5 g/l of BaCl₂ is added and then 3 g/l of Na₂HPO₄; and
- first 3 g/l of Na₂HPO₄ is added and the 5 g/l of BaCl₂.

The results show that chromium was fully removed in both cases indicating that the order of addition is not important for the removal of chromium. However, for strontium removal, the first sequence gives slightly more removal percent (58.55%) than the second sequence (57.08%). In both cases, strontium concentration still remains high. To decrease strontium concentration, it was suggested to treat the wash wastewater sample with 4 g/l of BaCl₂ first and then with 4 g/l of Na_2HPO_4 . In this case, the final concentrations of strontium and chromium in treated concrete wash wastewater sample were 0.1615 and 0.0260 mg/l, respectively, which were below the allowable limits of the water environmental standards. The removal efficiency of both chromium and strontium was in excess of 99%. These results further indicate that 4.0 g/l of BaCl₂ and Na₂HPO₄ could be an effective option to reduce chromium and strontium concentrations to environmentally acceptable levels. In this study, it was also found that a time of 10 min was sufficient for precipitation to reach equilibrium.

Since original concrete wash wastewater sample has pH 12.28 it is of prime interest to reduce the treated effluent to pH 6–8 to meet the environmental disposal limits. Also, the results indicated that use of 4 g/l Na_2HPO_4 would reduce solution pH to

Table 8 Effect of mixing time on quality of wash water

Mixing time (min)	Sr (mg/l)	Sr removal (%)	Cr (mg/l)	Cr removal (%)
15	4.34	64.45	0.00	100.00
30	4.44	63.63	0.00	100.00
45	4.38	64.12	0.00	100.00
60	5.03	58.80	0.00	100.00
75	4.59	62.40	0.00	100.00
90	4.92	59.70	0.00	100.00
120	5.47	55.19	0.00	100.00

about 10. Therefore, we evaluated the possible use of CO_2 bubbling to further reduce pH to acceptable levels. In the experiment, CO_2 was bubbled for 8 min at a flow rate of 4 l/min. As a result, pH in the treated concrete wash wastewater decreased to about 7 once in contact with CO_2 bubbling. As a result to pH decrease new minerals are formed as shown in Fig. 10 and precipitation increases leading to less residence time in the settling tank.

3.4. Settling conditions

The effect of time on settling and the settling velocity were studied. The settling behavior of treated wash wastewater sample was observed through settling tests. After elapsed time of 20 h, the height of Na₂HPO₄ was 20 ml, while the cylinder of BaCl₂ was not clear and has some turbidity and become clear after 24 h. It was observed that at the beginning of the experiments, the mixtures were extremely turbid. These results show that the settling velocity was very

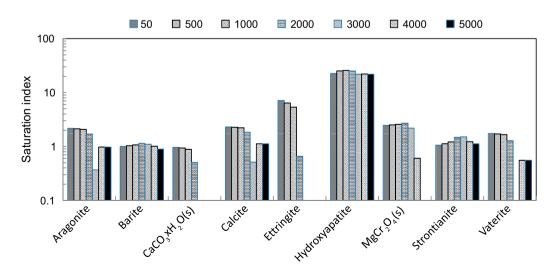


Fig. 9. Effect of Na₂HPO₄ dosage on type of precipitated minerals.

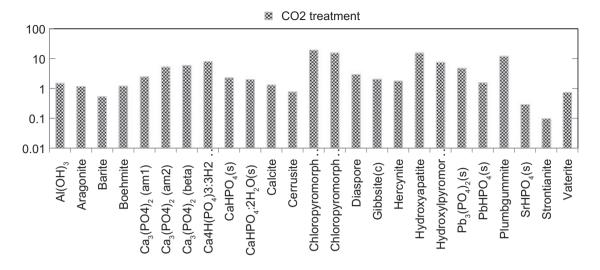


Fig. 10. Effect of CO₂ treatment on type of precipitated minerals.

small and the particles need at least one day to settle. Therefore, the results reveal the need of having a settling tank following the mixing process. The sludge quantities generated by the treatment processes are small. The mass of sludge for 100 ml of concrete wash wastewater sample after mixing and precipitation was about 1 g for the case of Na_2HPO_4 as well as for $BaCl_2$ case.

4. Conceptual design of the treatment plant

A typical RMC wash wastewater treatment plant process is proposed in Fig. 11. The four primary components of a conceptual treatment plant are the collecting tank, the two mixing tanks, and the settling tank.

The onsite concrete wash wastewater treatment system design shall vary according to the site and the

Ready-mix truck

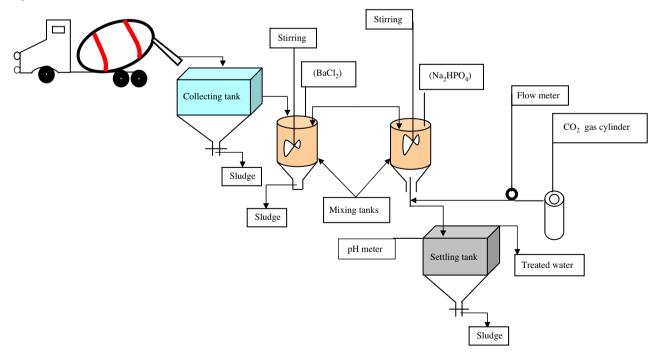


Fig. 11. Conceptual design of RMC wash wastewater treatment plant.

requirements. About 58 RMC batching plants were identified and were operational in Dubai Emirate with an average of 35 truck mixers. Assuming the maximum amount of water used per day for washing would be 150 l per truck, the maximum wash wastewater generated from each company per day would be about 5,250 l if each plant is considered to operate at its maximum capacity. Therefore, the wash wastewater treatment plant is with a total capacity of a maximum of 5,250 cubic meter of wash wastewater per day.

Comparing the existing handling and treatment practices in Dubai Emirate with the concrete wash wastewater treatment plant proposed here, the proposed system is superior for using only two chemical reagents to lower the concentrations of chromium and strontium to the acceptable disposal limits instead of using three chemical compounds (in Dubai treatment process) to lower only chromium concentration. As such, the capital cost of the proposed system is expected to be significantly less than the current adapted practice. Moreover, it is expected that the proposed system minimizes the operating costs since it utilizes four primary components instead of six chambered tanks used in current treatment system adapted by Dubai Municipality that even lacks the removal of strontium.

5. Conclusion

The results of this study revealed that RMC wash wastewater could be treated with the use of three treatment processes. In the first process, barium chloride was used to remove chromium to below acceptable limit whereby chromium concentration was not detected, i.e. 100% removal efficiency was achieved. In the second process, disodium hydrogen phosphate was used to remove strontium from wash wastewater to concentration level of 0.063 mg/l. Finally, in the third process, carbon dioxide was used to reduce treated solution pH to less than 8, whereby the treated wastewater would be accepted for disposal. The proposed removal system is expected to have less capital and operational costs than those of the present treatment system adapted by Dubai Municipality that even lacks the removal of strontium.

Other than proposing a suitable and economic method to treat the RMC wash wastewater, thermodynamic modeling was used to explain the experimental results related to the effect of BaCl₂ dosage on removal efficiency of strontium and chromium via the used model, the speciation of various compounds and the precipitated forms were also explained.

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