



Calcium silicate hydrate (CSH) from Egyptian heap fired rice straw ash (RSA). Preparation, characterization & some application

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ABSTRACT

Some Calcium silicate hydrates (CSH) were obtained by the reaction of calcium hydroxide and silicic acid prepared from silica present in the ash remained after heap burning rice straw. Either pure CSH or CSH with carbon and other compounds present in the ash and insoluble in sodium hydroxide solution can be prepared by this technique. The obtained calcium silicate hydrates were characterized by IR and XRD analysis; some heavy metals present in waste water and underground water were efficiently removed by them. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Rice straw ash;
Hydrothermal;
Calcium silicate hydrates;
IR and XRD analysis;
Removal of heavy metals.

INTRODUCTION

Burning of rice straw which is an agricultural waste available in large quantities in Egypt is a potential source of heat energy while the remaining residue (ash) is very rich in silica. The amount and crystallite state of the silica present in this ash depend upon the firing temperature, duration and air availability. Heap firing of rice straw leads to the formation of an ash rich in amorphous silica^[1-3].

There are many available data in the literature concerning burning agricultural wastes to produce ashes rich in silica which are used as mineral admixtures in concrete. Also, preparation of CSH by the reaction between pure silica and calcium hydroxide had been extensively studied^[4-6].

On the other hand there is no available data in the literature concerning heap firing of rice straw or prepa-

ration of CSH from the ash remained after firing rice straw or other agricultural wastes.

The aim of the present work was to prepare calcium silicate hydrate from the ash that remained after firing rice straw. This study also include characterization and assessing the possibility of using the obtained CSH to remove heavy metals from waste water and underground water.

EXPERIMENTAL

Preparation of CSH free from carbon and other RSA residues insoluble in NaOH solution

50g of RSA was added to about 200ml (0.8M) NaOH solution followed by boiling for 4 hrs, since previous experiments proved that under these conditions the mass of dissolved silica in NaOH solution was at its maximum value^[7]. The reaction mixture was then filtered

off while hot to separate the residual solids to obtain clear solution of sodium silicate. The filtrate was a clear colorless solution having a pH value of 9.9.

Silicic acid was then obtained by adding concentrated HCl solution drop by drop to the filtrate solution till reaching pH 7.5, and keeping the mixture at this pH during the reaction period. Calcium hydroxide solution was then added drop wise to this solution containing silicic acid while boiling on a hot plate with continuous stirring using a magnetic stirrer for 2 hrs. The final mixture was then filtered to separate calcium silicate hydrate from solution. The separated solid (CSH) was washed with distilled water and dried. The dried solid material was a very fine white powder, XRD, and IR tests were conducted on this solid material.

Preparation of CSH with carbon and other RSA residues insoluble in NaOH solution

Samples of calcium silicate hydrate with carbon and other RSA residues insoluble in NaOH solution were prepared from rice straw ash through the following steps: A certain mass of RSA was added to ~200ml of 0.8M NaOH solution. Mass of RSA added depends upon the state of RSA i.e. either heap or control fired. This mass was determined by the mass of this ash soluble in 0.8M NaOH solution.

Mixture of RSA and NaOH solution was then boiled for 4 hrs, then concentrated hydrochloric acid solution was added, drop wise to the boiled mixture till reaching a pH value of 7.5. This means that all sodium silicate had been acidulated to give silicic acid. And the precipitated silicic acid constitutes a gray. The mixture of carbon, and other residues insoluble in NaOH solution were still contaminated with the prepared CSH. The obtained solid material was washed and dried then subjected to XRD, and -R analysis.

Utilization of the produced CSH in the removal of Fe³⁺ and Mn²⁺ ions from underground water

Underground water samples were collected from different locations within the Delta region. All samples were filtered off and acidified with concentrated HCl to pH 2 then quickly introduced into plastic vessels at a temperature of 20-25°C. Suspended matters were determined by filtering 1000cm³ of the untreated water sample using a sintered glass G4 and weighing the residue after drying at 120°C for 2 hrs.

Dissolved oxygen (DO)

Dissolved oxygen (DO) was determined by Winkler method^[8], Dissolved oxygen was stabilized in field using manganese sulfate solution in presence of ammonia buffer. The formed managing compound was treated with H₂SO₄ and KI and the liberated iodine was titrated against K₂S₂O₃.

Total alkalinity

Total alkalinity (mg CaCO₃/L) was determined according to the method described by Strickland and Parsons^[8].

Total dissolved salts (TDS)

Total dissolved salts (TDS) of the water samples were determined by weighing the residue left after complete drying of 100cm³ of the water sample at 120°C for 2 hrs.

The reactivity of the produced material (CSH) towards heavy metals removal from aqueous solutions was also assessed. This was accomplished as follows: 100 mg of CSH was added to 100ml of the tested water sample and the pH value was again controlled. The sample was stirred for 30 min. and filtered off. The filtrate was subjected to ASS and determining the concentrations of Fe³⁺ and Mn²⁺ ions.

RESULTS AND DISCUSSION

Investigation of calcium silicate hydrate (CSH) prepared from rice straw ash (RSA)

Infrared spectral analysis

As has been mentioned above, calcium silicate hydrate (CSH) was prepared by the reaction between calcium hydroxide Ca(OH)₂ and SiO₂ from RSA, CSH was prepared in two different forms, CSH freed from carbon and other undissolved matters insoluble in NaOH solution, and CSH prepared in presence of all these matters. The main factors found to affect this reaction are, the temperature of the reaction medium, the time of the reaction, and stirring. It is very important to study the solubility of carbon in calcium silicate hydrate prepared, and in what form it is found.

For these reasons infrared absorption spectra measurements and X-ray diffraction analysis were carried out on the reaction products, the results of these mea-

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TABLE 1 : CSH samples and reference samples (L,C,H and S)

L	440	523	540	850	872	905	922	939	1000	1035	1430	1490		
C	440	500	520	570	820	860	925	940	950					
H	453	512	530	706	796	906	935	966	1020	1034	1445	1610	3635	
S	463	534	583	667	720	775	832	873	898	980	1007	1040	3400	
1	225	462				875	965	1983	2928	3439	1424	1632	3634	
2	225	454	667	964							1485	1644	3443	
3	225	318	459	656	873	965			1790	3444	1484	1632	3633	
4	223	276	305	480	707	876	964		2515	3442	1449	1793	3634	
5	225	454	667	964							1485	1644	3443	
6	220	315	452	665	708	873	969	1441	1631	1792	2335	3432	3626	
7	222	306	454	663			968	1983	2337	1792	1434	1638	3424	
8	221	303	454	658			970	2355	2933	3627	1433	1631	3436	
9	221	305	454	656		969				2355	1425	1631	3427	
10	222	309	458			1795	1981	3442	1048		1434	1631	3635	
11	221	453	660			968	1987	2358	2851	2926	1424	1632	3424	
12	223	305	476	658	708	873	967	1485	3626	1793	2335	1631	3424	
Assi.	CaO bending		Si-O-Si bend.									δOH	δOH	vOH

measurements and the analysis for these results are found in TABLE 1.

The IR absorption spectra of CSH samples figure 6 shows three bands at 1100-1200 (broad), 800, and 463 cm^{-1} assigned to longitudinal SiO_2 lattice vibration^[9,10] symmetric Si-O-Si stretching^[11] and Si-O-Si bending respectively. Weak absorption bands were also observed at 1790, 2335, and 2928 cm^{-1} which are assigned to symmetric and asymmetric stretching (ν_{as}) vibrations respectively^[12]. The absorption bands at 3449 cm^{-1} are due to $\nu(\text{OH})$. The band at 1640 cm^{-1} is a combination tone due to $\delta(\text{OH})$, and the SiO_2 overtone. The uniformity of the figure gives the indication that CSH prepared its type from the mode of vibration depends mainly on the source of SiO_2 used.

CSH from heap fired rice straw ash have the same characteristic peaks at 221, 968, 1485, and 3427 cm^{-1} which are assigned to symmetric CaO stretching symmetric Si-O-Si stretching and Si-O-Si bending respectively. Weak absorption bands were also observed at 1790, 2335, and 2928 cm^{-1} which are assigned to asymmetric stretching (ν_{as}) vibrations respectively^[12]. Longitudinal SiO_2 lattice vibration at 454 cm^{-1} was found but very weak. As could be seen from these results and from the literature some expected peaks disappears e.g. CaO stretching at 1410 cm^{-1} and CaO bending at 810 cm^{-1} some other peaks were shifted as CaO from 874 cm^{-1} to 810 cm^{-1} and SiO_2 from 1200 cm^{-1} to

968 cm^{-1} ^[13,14]. Based on these changes in the IR band positions the formation of CSH can be confirmed from the IR patterns.

X-Ray diffraction analysis (XRD)

The XRD measurements for three samples of (CSH) prepared from heap fired RSA and obtained under different conditions were carried out in order to investigate the changes occurring due to their formation reactions.

Figure 1 shows the result of these measurements. There are two forms of CSH, these two forms have chemical composition as CSH (1) (0.8-1.5 CaO. SiO_2 . 0.5-2.5 H_2O) and CSH (2) (1.5-2.0 CaO. SiO_2 . 1-4 H_2O). natural plombierite is closely similar but gives no basal X-ray diffraction.

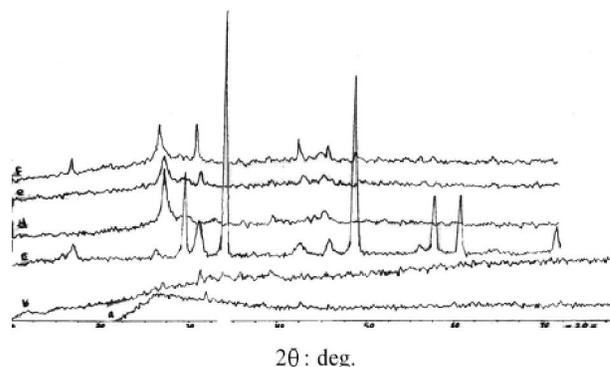


Figure 1 : XRD patterns for CSH samples. a, b ash samples, c CaO sample, d, e CSH samples and f CSH with Fe^{3+}

TABLE 2 : Removal of Fe³⁺ ions by CSH

Time hr	pH	Meas. conc.	Abs. conc.	%abs.
0	1.9	43.55	-	-
0.5	11.25	0.25	43.3	99.46
1.0	11.24	0.26	43.29	99.4
1.5	11.15	0.21	43.34	99.5
2.0	11.24	0.21	43.34	99.5
3.0	11.23	0.23	43.32	99.47
4.0	10.8	0.07	43.48	99.84
For underground water				
4.0	11.72	Nil	5	100 %

TABLE 3 : Removal of Fe³⁺ ions by ash and CSH from silica gel

Ash				
Time hr	pH	Meas. conc.	Abs. conc.	%abs.
0	1.9	50.0	-	-
0.5	2.33	16.17	27.38	62.87
4.0	11.15	0.40	43.15	99.08
CSH from silica gel				
4.0	11.25	0.19	43.36	99.56

The crystal form Crumpled foils (semi-crystalline) and basal spacing of CSH (1) varies with both water content and Ca/Si ratio hence several varieties exist. Powder data relate to fiber bundles. Some other varieties give powder patterns close to that of CSH (1). The basal spacing, if it occurs, is always about 10Å^[15,16]. From figure 1 and CSH (2) were formed and also the two forms are convertible. This is due to two main factors, the water content, and Ca/Si ratio.

Application of CSH obtained from RSA to the removal of Fe³⁺ and Mn²⁺ ions from underground water

The main water quality properties was examined before treatment with CSH and the results were TDS (3.090g dm⁻³), TSM (0.106g dm⁻³), DO (4.49mg O₂ dm⁻³), and total alkalinity determined (153.5mg CaCO₃ dm⁻³) respectively. This reveals that treatment with CSH has no appreciable effect upon the main water properties. The allowed concentrations of iron, and manganese are 200 and 50µg/l respectively, according to health related guide level (HRGL).

CSH was used for the treatment of wastewater and underground water to remove Mn²⁺ and Fe³⁺ as examples for divalent and trivalent metal ions. The results for this treatment are shown in TABLE (2, 3 and 4).

TABLE 4 : Removal of Mn²⁺ ions by CSH

Time hr	pH	Meas. Conc.	Abs. conc.	% abs.
0	8.52	9.958	-	-
1.0	11.74	0.021	9.937	99.79
2.0	11.62	0.029	9.929	99.71
2.5	11.44	7.21	21.11	74.5
3.0	11.61	0.017	9.941	99.83
4.0	11.55	0.015	9.943	99.85
4.0	10.8	0.07	43.48	99.84
For underground water				
4.0	11.72	0.017	0.033	99

TABLE 2 and 3 give the removal of Fe³⁺ ions from water by using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Fe³⁺ ions from water by the prepared CSH was very efficient as almost 99.8% from the initial amount of the metal ion in the solutions were removed.

TABLE 4 includes the data for the removal of Mn²⁺ ions from water using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Mn²⁺ ions from water by the prepared CSH was very efficient as almost 99.85% of the initial amount of the metal ion in the solutions were removed.

CONCLUSION

Calcium silicate hydrates (CSH) was prepared by two procedures, preparation of CSH free from carbon and other insoluble matters in NaOH solution, and preparation of CSH in presence of these matters. The characterization of these prepared materials using IR, and XRD measurements. The prepared CSH was utilized in the removal of Fe³⁺ and Mn²⁺ from waste water and underground water treatment; as these two ions are the most abundant in underground water.

The removal process was found to be very efficient as the prepared CSH removed about 99.84 % of Fe³⁺ from waste water and most of that present in underground water. The amount from Mn²⁺ ions removed from waste water samples reached about 99.85 %, and most of that present in underground water.

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SYMBOLS

- (1) CSH sample from sodium silicate obtained from RSA treated with HCl and calcium hydroxide solution, boiled and stirred for 1 hr.
- (2) CSH sample from commercial sodium silicate treated with HCl and calcium hydroxide solution, boiled and stirred for 1 hr.
- (3) CSH sample from silica gel and CaO powder and boiling in distilled water for 1 hr.
- (4) Washed CSH sample from no. (1) in 800 ml distilled water and boiling for 2 hrs.
- (5) Washed CSH sample from no. (2) in 800 ml distilled water and boiling for 2 hrs.
- (6) Washed CSH sample from no. (3) in 800ml distilled water and boiling for 2 hrs.
- (7) CSH sample from control fired ash(500°C) and calcium hydroxide solution.
- (8) CSH sample from heap fired RSA and calcium hydroxide solution, boiled for 4 hrs.
- (9) CSH sample from heap fired, washed RSA and calcium hydroxide solution, boiled for 4 hrs.
- (10) CSH sample from heap fired, washed RSA and calcium hydroxide solution, while boiling for 2 hrs.
- (11) CSH sample from heap fired, washed RSA and calcium hydroxide solution, boiled for 5 hrs.
- (12) CSH sample from heap fired, washed RSA and calcium hydroxide solution, stirred and boiled for 4 hrs.

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