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

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 preparation 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 4hrs, 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 continues 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 acidculated 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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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 463cm\(^{-1}\) assigned to longitudinal SiO\(_2\) lattice vibration\[^{[9,10]}\] and Si-O-Si bending respectively. Weak absorption bands were also observed at 1790, 2335, and 2928cm\(^{-1}\) which are assigned to symmetric and asymmetric stretching (v\(_{as}\)) vibrations respectively\[^{[12]}\]. The absorption bands at 3449cm\(^{-1}\) are due to \(\delta\)(OH). The band at 1640cm\(^{-1}\) is a combination tone due to \(\delta\)(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 3427cm\(^{-1}\) 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 2928cm\(^{-1}\) which are assigned to symmetric stretching (v\(_{as}\)) vibrations respectively\[^{[12]}\]. Longitudinal SiO\(_2\) lattice vibration at 454cm\(^{-1}\) was found but very week. As could be seen from these results and from the literature some expected peaks disappears e.g. CaO stretching at 1410cm\(^{-1}\) and CaO bending at 810cm\(^{-1}\) some other peaks were shifted as CaO from 874cm\(^{-1}\) to 810cm\(^{-1}\) and SiO\(_2\) from 1200cm\(^{-1}\) to 968cm\[^{[13,14]}\]. 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\(_2\)O) and CSH (2) (1.5-2.0 CaO. SiO\(_2\). 1-4 H\(_2\)O), natural plombieriteis are closely similar but gives no basal X-ray diffraction.

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

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Assi. CaO bending Si-O-Si bend. \(\delta\)OH \(\delta\)OH vOH

Figure 1: XRD patterns for CSH samples. a, b ash samples, c CaO sample, d, e CSH samples and f CSH with Fe\(^{3+}\).
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The crystal form Crumpled foils (semi-crystalline) and basal spacing of CSH (1) varies with both water content and Ca/Si ratio. 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 Fe\(^{3+}\) and Mn\(^{2+}\) ions from underground water**

The main water quality properties was examined before treatment with CSH and the results were TDS (3.090 g dm\(^{-3}\)), TSM (0.106 g dm\(^{-3}\)), DO (4.49 mg O\(_2\) dm\(^{-3}\)), and total alkalinity determined (153.5 mg CaCO\(_3\) 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 50 µg/l respectively, according to health related guide level (HRGL).

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

**TABLE 2 : Removal of Fe\(^{3+}\) ions by CSH**

<table>
<thead>
<tr>
<th>Time hr</th>
<th>pH</th>
<th>Meas. conc.</th>
<th>Abs. conc.</th>
<th>%abs.</th>
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<td>43.48</td>
<td>99.84</td>
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</table>

For underground water

| 4.0     | 11.72| Nil        | 5          | 100 % |

**TABLE 3 : Removal of Fe\(^{3+}\) ions by ash and CSH from silica gel**

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<th>%abs.</th>
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**TABLE 4 : Removal of Mn\(^{2+}\) ions by CSH**

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<td>99.84</td>
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</table>

For underground water

| 4.0     | 11.72| 0.017      | 0.033      | 99    |

TABLE 2 and 3 give the removal of Fe\(^{3+}\) ions from water by using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Fe\(^{3+}\) 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 Mn\(^{2+}\) ions from water using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Mn\(^{2+}\) 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 Fe\(^{3+}\) and Mn\(^{2+}\) 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 Fe\(^{3+}\) from waste water and most of that present in underground water. The amount from Mn\(^{2+}\) ions removed from waste water samples reached about 99.85%, and most of that present in underground water.

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To whom all assists me and encourage me forward
Current Research Paper

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at all

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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 800 ml 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.

REFERENCES