Solidification of cement kiln dust using sulfur binder

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ABSTRACT

The present study aims to offer a new methodology for consuming two industrial wastes; sulfur, from petroleum and natural gas industries, and cement kiln dust (CKD), from Portland cement industries, in construction industry. Sulfur solidified cement kiln dust material (SSCKDM) was manufactured by mixing molten sulfur, treated sulfur, CKD and sand at a controlled temperature in excess of 120 °C. The hot mixture was subsequently cast and shaped into the desired mold and was then allowed to solidify at a specified cooling rate. Solidified materials were immersed for time periods up to 28 days in distilled water at different temperatures of 25 and 60 °C, sea water, and acidic and basic universal buffer solutions of pH4 and pH9, respectively. Solidified material performance as function of time and type of aqueous solution exposed to was evaluated in view of compressive strength variations and leachability of metal and heavy metal ions.

The results indicated that the solidified articles exhibit homogenous and compact internal microstructure with excellent mechanical properties. However, it showed durability problem upon exposure to aqueous solution environments due to the initial chemical composition of the CKD, whose leached test showed release of relatively high amounts of sulfates and alkali metals. Durability of SSCKDM articles in relation to strength reduction and crack formations control was improved by addition of glass fiber while, the use of anti-leaching agent such as anhydrous sodium sulfide resulted in reduction of leached heavy metals without any measurable decrease in leached amounts of alkali metals and anions from the solidified matrix. Furthermore, based on leachability index method of calculation, potential chemical mobility of metal and heavy metal ions from the solidified matrix was characterized as medium.

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1. Introduction

During recent years there has been a growing interest in the reuse of waste materials and by-products in construction industries. Cement Kiln Dust (CKD) is a by-product of cement manufacturing process. The dust is mainly a blend of partially calcined and un-reacted raw feed, clinker dust, alkali sulfates, halides and ash. Cement manufacturing plants generate about 30 million tons of CKD worldwide per year [1]. While modern dust-collecting equipment is designed to capture virtually all CKD and much of this material can today be returned to the kiln, for various reasons, a significant portion, in some cases as much as 30–50% of the captured dust, must be removed as industrial waste [2,3]. As a result in the United States of America, more than 4 million tons of CKD, unsuitable for recycling in the cement manufacturing process, require annual disposal [4]. As the volume of CKD generated increased, the cost associated with its disposal becomes larger and the interest in finding applications to recover and reuse of CKD becomes greater.

The dominance of many countries in the petroleum and natural gas industries and increased environmental awareness and regulations around the world have created a tremendous increase in recovered sulfur production throughout the world. An example of a country with large production and limited consumption is Canada. As in other developed countries, Canada limits the level of sulfur allowable in gasoline and other automotive fuels and SO_2 emissions at petroleum refineries.

Global sulfur demand has been relatively stagnant at about 57 million metric tons per year over the last decade. Based on new regulations limiting sulfur content in diesel and gasoline, the current small global surplus in sulfur supply is projected to reach between 6 and 12 million metric tons by 2011 [5], or between 10 and 20% of demand. This projected surplus represents obvious challenges to existing producers, potentially leading to drastically reduced sulfur prices, and even the possibility of costs to producers for disposal of the surplus in some regions. On the other hand, the surplus may also represent opportunities for new uses of sulfur, driven by these very same reductions in sulfur price that can make new uses more economically feasible and attractive.

Even with relatively small surpluses, the oil and gas industry has already experienced strains on sulfur storage facilities. Sulfur is being stored on site in block, granular or palletized form, or

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Fig. 1. Sulfur market dynamics [6].
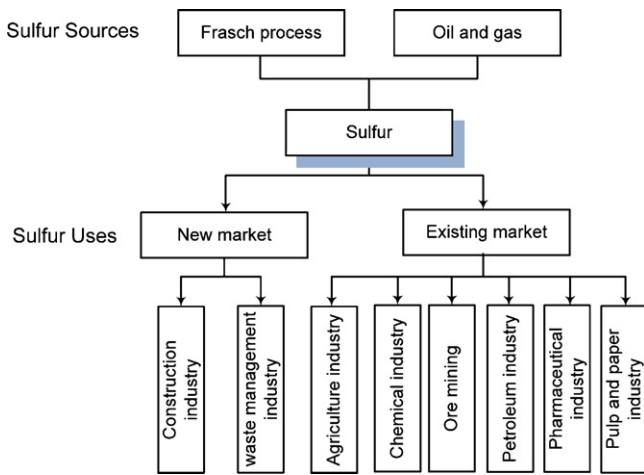

Fig. 2. SEM image of fresh cement kiln dust (CKD).

molten (very expensively) in rail tank cars because there is insufficient storage capacity to handle sulfur generation at refineries and gas processing plants.

There is a clear trend of the dramatic change in the global sulfur industry over the last decade. Sulfur consumption is dominated by a number of large-scale uses, with several complex interactions that complicate the future outlook for demand. Thus, sulfur is used to produce sulfuric acid, one of the world's largest volume chemical commodities, but this use competes with sulfuric acid recovered from ore smelting. Uses of sulfuric acid include processing phosphate rock and ore leaching in metallurgical processing (a growing market). There are number of other uses for sulfur [6] such as inclusion in pigments, pesticides, and rubber vulcanization and as an agricultural nutrient (Fig. 1).

The challenges facing the sulfur industry are unique. The sulfur industry is confronting the question of what to do with all the sulfur it produces. Current production exceeds consumption, but environmental regulations continue to increase with little growth in sulfur uses. The 21st century sulfur industry will need to expand sulfur consumption in non-traditional markets and find acceptable ways to dispose of un-needed sulfur without compromising environmental protection. New markets must be found for sulfur to avoid disposal crises.

Research and development of sulfur polymer concrete (SPC) are in progress to explore potential markets for the use of elemental sulfur present in many countries as a byproduct of oil and gas industry. SPC material is a thermoplastic material developed by the U.S. Bureau of Mines in 1972 to use by-product or waste sulfur as an alternative to hydraulic cement for construction applications and significantly improves the stability of the product [7]. SPC consists of modified sulfur, physical stabilizers and aggregates. As in Portland Cement Concrete (PCC), it is possible to use naturally occurring heavy aggregates, e.g., sand, gravel, stone chips or ballast. Synthetic aggregates from waste material like crushed cinders, brick dust, foundry sand, crushed quartzite gravel, crushed limestone, siliceous tailing sand, expanded shale, expanded clay, crushed barite, crushed brick, crushed PCC, and crushed granite could also be used in manufacturing SPC [8–10]. Mohamed and El Gamal [11,12] have utilized fly ash to produce sulfur cement and durable sulfur polymer concrete. The type and quality of aggregates have a substantial effect on the properties and durability of the produced SPC [6].

The preceding highlights the problems associated with CKD and sulfur disposals. This study aims to find a sustainable utilization to these by products in waste management industry. Therefore, the study is designed to contribute to the new uses of sulfur in
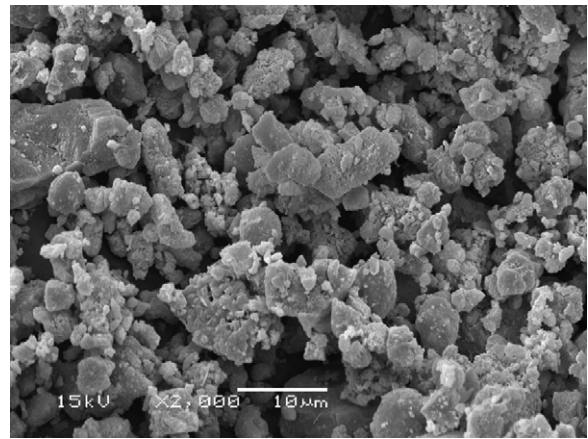
hazardous solid waste management field via solidifying CKD using sulfur as a binder material. The performance of solidified articles exposed to different types of aqueous solutions has been evaluated through examination of compressive strength and leachability of metal and heavy metal ions.

2. Materials and methods

2.1. Raw materials

Cement Kiln Dust utilized in this study was obtained from Al Ain cement factory, Al Ain, UAE. Table 1 shows the chemical composition of major oxides present in CKD. The results indicated that the major constituents are compounds of lime, iron, silica and alumina. The percent loss on ignitions (LOI) determined from thermo-gravimetric analysis (TGA) is 25.17 and pH is around 12. Fig. 2 shows the microstructure determined by using the scanning electron microscope. The CKD particles are characterized as coarse, irregular and random with mean particle size of approximately 5–7 μm. Fig. 3 shows the cumulative grain size distribution.

The used desert sand was obtained from a sandy dunes quarry in Al Ain area, UAE. The most common constituent of sand is silica (silicon dioxide), with specific gravity of 2.58 g/cm^3, usually in the form of quartz. Chemical analysis using ICP-AES indicated that the sand mainly consists of oxides of silica, calcium, magnesium, iron, aluminum and potassium. Thermal analysis indicated that LOI of desert sand is 6.016%. The sand was screened to obtain grain sizes
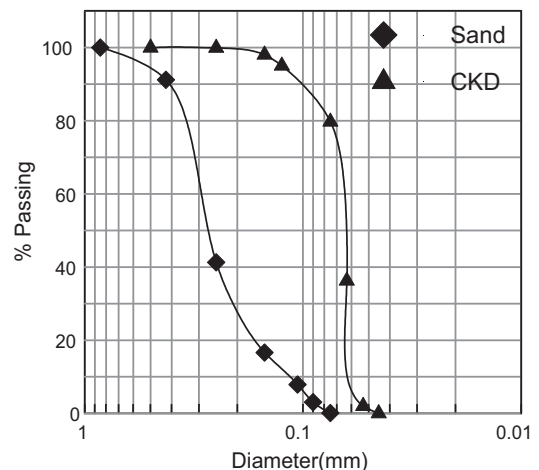

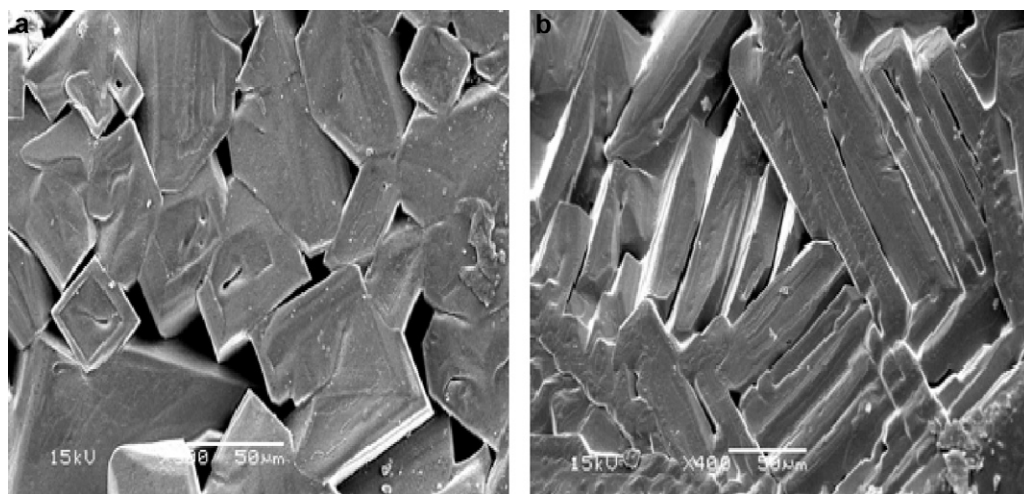**Fig. 3.** Grain size distributions of cement kiln dust (CKD) and sand.

Fig. 4. SEM images of (a) crystalline morphology of pure elemental sulfur, (b) treated sulfur.

ranging from 0.08 to 0.43 mm. Fig. 3 shows the cumulative grain size distribution.

Granular elemental sulfur, with purity of 99.9%, was obtained from Al Ruwais refinery, UAE. Elemental sulfur was treated by means of bitumen as olefin hydrocarbon polymeric material, which is black oily, viscous, with specific gravity of 1.0289 g/cm^3, kinematics viscosity of 431 cSt at 135 °C and softening point of 48.8 °C. The elemental analysis of the used bitumen indicated that it contains 79% carbon, 10% hydrogen, 3.3% sulfur and 0.7% nitrogen.

The used glass fiber was chopped strand Canada glass fiber ranging from 6 to 14 mm in length.

2.2. Equipments

The following equipments were used in this study.

1. Elemental analyzer, Finnigan Flash EA1112 CHN/S, for the determination of C, H, N and S.
2. Strength testing machine with maximum load of 200 KN, for compressive strength measurements.
3. Scanning electron microscopy (SEM) JSM-5600 JOEL microscope, equipped with an energy dispersive x-ray detector (EDX), for microstructure characterization.
4. Inductively Coupled Plasma-Atomic Emission (ICP) Spectrometry (ICP-AES) VISTA-MPX CCD simultaneous, for determination of alkali metals and heavy metals leached from the solidified matrix.
5. Ion-chromatography (IC) DIONX IC 90, for determination of leached anions.

2.3. Reagents

2.3.1. Leaching agents

For leachability testing of solidified articles, the following aqueous solutions were used: (a) distilled water at different temperatures of 25 and 60 °C; (b) sea water; and (c) acidic and basic solutions of pH4 and pH9. Since the leachability testing was done

for long time periods stable acid and basic solutions (universal buffer solutions) were prepared by mixing equal volumes of acids (acetic acid, phosphoric acid, and boric acid) in bottles. The total molarity of the acid mixture was maintained at 0.4 M for the three acids. The desired pH was reached by mixing the acid mixture with the required 1 M sodium hydroxide solution. A constant ionic strength of each buffer solution (pH4 or pH9) was maintained and adjusted using pH meter. These buffer solutions were used instead of that described by [13].

2.3.2. Precipitates or anti-leaching agent

Anhydrous sodium sulfides in amounts of 1–10 wt% were used to reduce the solubility of metal and heavy metal ions present in CKD.

2.4. Preparations of sulfur solidified CKD materials

2.4.1. Sulfur treatment

Sulfur was treated by mixing elemental sulfur and a chemical stabilizer (bitumen) to form a sulfur-containing polymer [11,12]. To facilitate the compatibility between elemental sulfur and the bitumen, emulsifying agent was used [14]. The mixing process was maintained at about 140 °C for a period of 45–60 min. The development of the reaction is followed by monitoring the changes in viscosity and homogeneity of the mixture. The final product is a sulfur-containing polymer, which on cooling possess glass like properties. Detailed description of the preparation can be found in [14].

2.4.2. Sulfur solidified CKD materials

Sulfur solidified CKD materials (SSCKDM) were prepared according to the procedure described in [11,12,14,15] for mixing and placing sulfur concrete. The preparation of the solidified articles was carried out by preheating the aggregates (CKD and sand dunes) prior to the mixing step to a temperature of 120–200 °C, then mixing the preheated aggregate with treated sulfur in a melted state in a suitable mixer at about 120–140 °C until a substantially

Table 1
Chemical composition of CKD and sand.

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	K$_2$O	Na$_2$O	LOI
CKD	12.63	2.26	2.08	46.47	0.89	1.56	1.78	0.25	25.17
Sand	74.4	0.47	0.676	16.35	1.158	–	0.13	–	6.016

Oxides values expressed as weight percent. LOI indicates percentage loss on ignition determined using thermal gravimetric analysis (TGA).

homogeneous mixture is obtained, the temperature being maintained throughout the mixing. The hot mixture was subsequently cast and shaped into the desired mold shape as cylindrical and cubes. Furthermore, the cooling step may cool the molten sulfur mixture to the temperature sufficient to harden the encapsulated materials. However, preferably the cooling step comprises cooling the treated sulfur to a temperature of less than about 70 °C. The cooling step may be performed at any time throughout the process as necessary to produce the hardened material.

2.5. SSCKDM composition requirements

2.5.1. Mix design and strength improvement

The desirable balance between (a) sulfur binder composed of treated sulfur and elemental sulfur, (b) the ratio of aggregates (CKD and sand) to sulfur binder, and (c) the amount of glass fibers as physical filler was studied with the purpose of improving the workability, specific gravity and mechanical strength of the SSCKDM.

2.5.2. Cooling rate

The mixture of the SSCKDM in its molten state was thoroughly mixed at 132–141 °C. The specimens were then casted in the preheated steel molds at approximately 138 °C. During pouring of the molten SSCKDM into the specified molds, the mixture was compacted by vibration for 10 s on a vibrating plate. The effect of cooling rate on microstructure of the formed SSCKDM was investigated.

2.6. Testing of SSCKDM durability

2.6.1. Effect of aqueous environments

Solidified specimens were casted and cured in air for 3 days, and then were immersed in four different solutions; de-ionized water at 25 and 60 °C, seawater, and acidic and basic universal buffer solutions of pH4 and pH9, respectively, for a period of 28 days. Compressive strength measurements were conducted after immersion in the previous solutions.

2.6.2. Leaching of CKD

The leaching test of CKD was carried out in accordance to the British Standard method [16], which designed to examine the short- and long-term leaching behavior of granular waste materials and sludge. As per the method the used liquid solution is de-ionized water at neutral pH. The CKD solution was prepared at liquid-to-solid ratio of 2 L/kg, shaken for 6 h, and then filtered. The solid residue was taken and mixed with water at liquid-to-solid ratio of 8 L/kg. The resulting mixture was further shaken for 18 h. The supernatant was then filtered with a 0.45 μm filter paper and then divided into two parts for analysis. The first part was measured by Ion-Chromatography (DIONEX IC 90) for the chloride and sulfate contents while, the second was acidified with nitric acid to pH < 2 for metal analysis. The concentrations of the leached metals, heavy metals and anions were analyzed using ICP and IC.

2.6.3. Leaching of SSCKDM

Leaching experiments were performed in accordance with the Accelerated Leach Test procedures that developed for evaluating potential leachability from solidified matrices [17]. The test protocol specifies changes in pH medium, temperature and testing time. The leaching of monolithic specimens instead of crushed waste forms was adopted in this investigation. Leaching experiments were performed by immersing the SSCKDM with dimension of 50 mm × 50 mm × 50 mm in a transparent container filled with 1 L of tested solutions (distilled water at different temperatures of 25 and 60 °C, sea water, acidic and basic universal buffer solutions of pH4 and pH9, respectively). Solutions were then analyzed in dupli-

Table 2
Chemical composition of the sulfur bitumen mixture.

Composition		Properties	
Material	Proportion (%)		
Sulfur	97.4 ± 0.48	Specific gravity	1.89 g/cm^3
Carbon	1.981 ± 0.074	Viscosity, at 135 °C	25 cP
Hydrogen	0.1 ± 0.067		

cates using ICP and IC to evaluate the leached metals and sulfates as function of time.

2.6.4. Precipitates or anti-leaching agent

The effect of inclusion of precipitates or anti-leaching agent on the mobility of metal and heavy metal ions from SSCKDM was studied. Anhydrous sodium sulfides in amounts of 1–10 wt% were added to reduce the solubility of metals in CKD. Treated sulfur and elemental sulfur were preheated to about 135 ± 5 °C then, CKD, sand and anhydrous sodium sulfide were added and thoroughly mixed till complete homogeneity. The homogeneous molten mixture was then poured into the desired mold. The mold was allowed to cool and the mixture solidifies thereby, immobilizing and encapsulating the metal ions present in the solidified matrix.

3. Results and discussion

3.1. Treated sulfur and SSCKDM

Table 2 shows the chemical composition of treated sulfur determined using CHN/S elemental analyzer. Addition of bitumen in amounts of 2.5–5 wt% to elemental sulfur initiates chemical reactions dependent on the bitumen content, heating temperature and reaction time [12]. Some competing reactions such as bitumen incorporation into sulfur molecules and/or de-hydrogenation with liberation of hydrogen sulfide could occur [6]. The reaction of sulfur with bitumen at 140 °C produces a mixture of polysulfide and free elemental sulfur, which held as monoclinic sulfur crystal. It is supposed that the growth of large crystals may be restricted because bitumen particles serve as nucleation sites that cause the formation of many small crystals instead of fewer large orthorhombic sulfur crystals, as shown in Fig. 4a and b. The resulting modified sulfur leads to sulfur solidified products that are not highly stressed and have good durability and corrosion resistance. Fig. 5 shows the SEM results of SSCKDM indicating that the internal structure is extremely homogeneous with high degree of packing.

3.2. Optimum mix design of SSCKDM

Optimum physical, chemical and mechanical properties of the SSCKDM articles are highly dependent on the amount of modified sulfur cement, ratio of sulfur binder to CKD, amount of fiber glass present, and cooling rate, which are discussed below.

3.2.1. Amount of modified sulfur cement

Compressive strength results of SSCKDM specimens indicated that the compressive strength decreased linearly with increasing the amount of modified sulfur cement as shown in Fig. 6a. Addition of polymerized sulfur increases the viscosity of the mixture hence, the crystal growth becomes difficult and its formation rate is reduced causing partial reduction in the resultant compressive strength [9]. The preferred amount of modified sulfur cement ranges between 0.25 and 0.35 wt (%) based on the total weight of the sulfur cement.
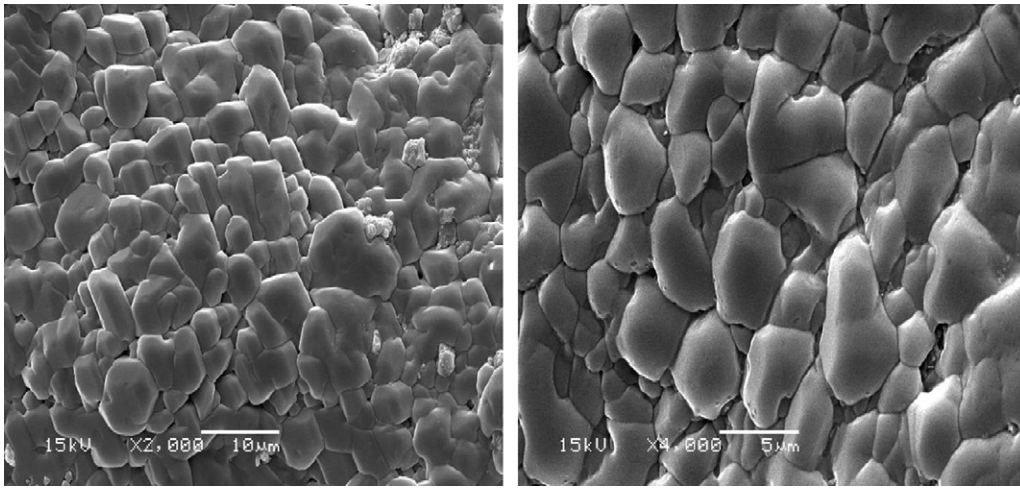
Fig. 5. SEM images of sulfur SCKDM showing the well compacted structure together with smooth closed surface.
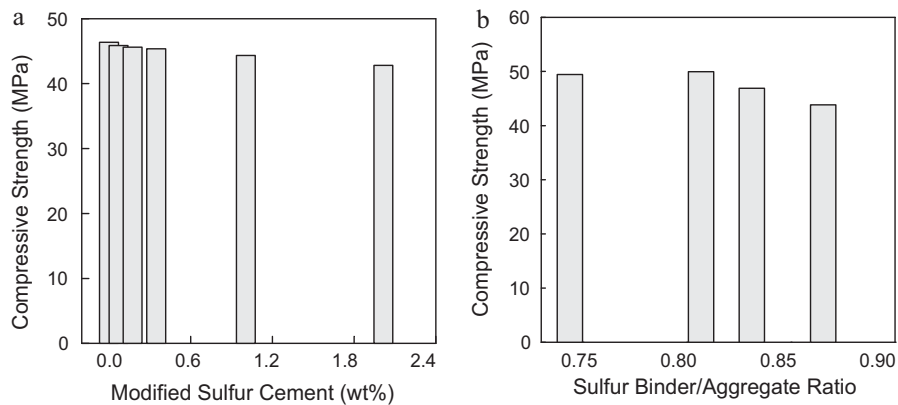

Fig. 6. Effect of the modified sulfur cement percentage and the ratio of sulfur binder to CKD on the compressive strength of sulfur SCKDM.

3.2.2. Ratio of sulfur binder to CKD

Proportioning and mixing CKD, sand and sulfur binder would affect the final quality and serviceability of the hardened mortar. For a given quality of sulfur binder, maximum compressive strength was achieved at certain optimum binder content. Fig. 6b shows the maximum compressive strength was obtained for sulfur binder/aggregates ratio of 0.8. On the other hand, utilization of larger sulfur binder/aggregates ratios resulted in reduction of the compressive strength that can be attributed to the formation of a thick layer of sulfur around the aggregate particles leading to formation of brittle products. In addition, the ratio of sulfur binder significantly influenced the rheological properties of the mixture, which is reflected in the compatibility, density and voids content of the resulting SSCKDM.

3.2.3. Addition of glass fiber

The influence of glass fiber addition on compressive strength development was investigated and the results are shown in Fig. 7. The results revealed that inclusion of glass fiber up to 0.35 wt% causes an increase in compressive strength. It was also observed that inclusion of glass fiber prevents chipping and flaking. However, inclusion of large quantities of glass fiber will tend to clump hence, reducing mixture workability and lowering its strength.

It is reported that inclusion of glass fiber will enhance the reinforced characteristics of the solidified matrix [18] and incorporation into the solidified matrix could be either in continuous lengths or in discontinuous (chopped) lengths. The filler combining step could be performed prior to or during the mixing step. In this study, both elemental and modified sulfurs are mixed first after that the CKD then other aggregates are added with the glass fiber. Fig. 8 shows uniform distribution of glass fiber with sulfur binder, CKD and sand.
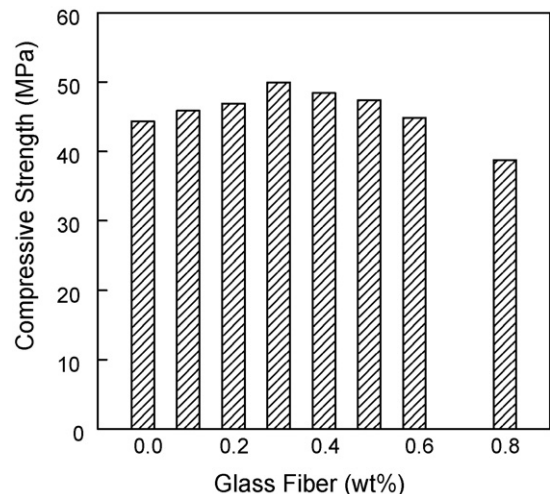

Fig. 7. Effect of glass fiber on the compressive strength of sulfur SCKDM.
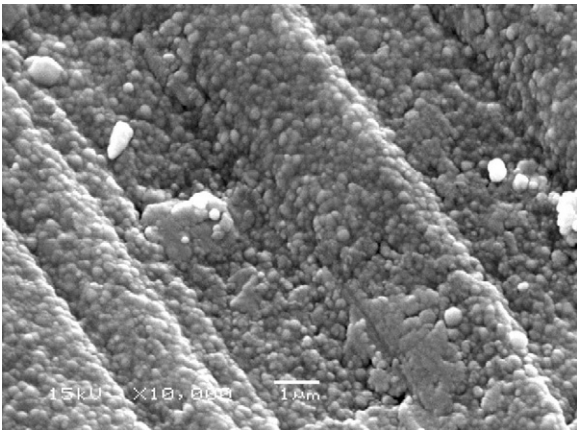
Fig. 8. SEM image of sulfur SCKDM reinforced with glass fiber.

3.2.4. Cooling rate

In the production of SSCKDM, the dried aggregates admixed with the molten modified sulfur and the molten mixture is then casted into molds and allowed to solidify by cooling. Experimental results indicated that the fast cooling rate of prepared articles in the order of 15–30 °C/min has contributed to the formation of hollow voids along the cylinder's axial centerline. This phenomenon is attributed to formation of a rigid layer on the exterior surface of the specimens due to convection. In turn, the solid exterior surface restricts the movement of the molten material at the center as it begins to solidify and shrink leaving a void in the center as shown in Fig. 9. Voids formation decreased with decreased cooling rate to 5 °C/min. Eventually, the optimum amounts of starting material preferably comprises mixing 40–45% by weight of the elemental sulfur, 30–40% by weight of sand, 20–25% by weight of CKD, 0.2–2% by weight of modified sulfur, and 0.3–0.5% of glass fiber, based on the total weight of the SSCKDM articles.

3.3. Durability performance

3.3.1. Assessment of physical and mechanical properties

Specimens made from SSCKDM were tested after immersion for a period of 28 days in different aqueous environments (de-ionized water at 25 and 60 °C, seawater, and acidic and basic buffer solutions of pH4 and pH9, respectively). Visual inspection indicated that surface texture exhibits many erosion sites and cracks after immersion in all solutions and was highly observed for the acidic solutions. Table 3 shows the compressive strength results of SSCKDM spec-
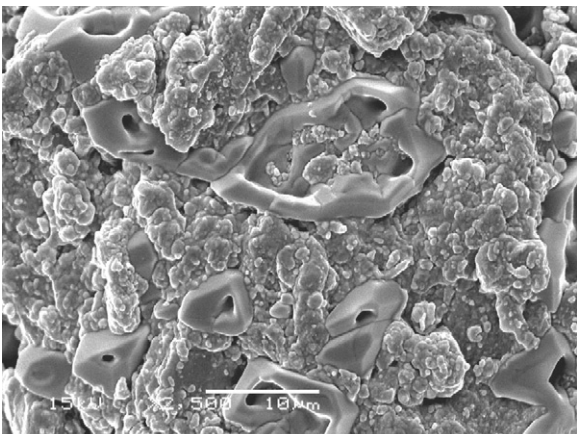
Table 3
Compressive strength of sulfur SCKD articles before and after addition of 0.35 wt% glass fiber, tested in different environments for a period of 1 month.

Tested solution	Compressive strength (MPa)	
	Without glass fiber	With glass fiber
Air	44	50
Water at 25 °C	30	41
Water at 60 °C	27	32
Seawater at 25 °C	29	36
Buffer solution of pH 9	24	34
Buffer solution of pH 4	19	23

imens before and after the addition of glass fibers. The results indicated that inclusion of glass fibers in SSCKDM has resulted in: (a) formation of products with minimum erosion sites hence, minimum potential for crack formations; (b) control of shrinkage cracks, improve material ductility and impact resistance; (c) reduction of linear shrinkage hence, shifting fracture mode from brittle/catastrophic to plastic/non catastrophic [19]; (d) increase of compressive strength of tested specimens in air; and (e) significant compressive strength reduction when solidified articles exposed to aqueous solutions.

Fig. 10 shows microstructure formation of SSCKDM after exposure to aquatic environment. The Figure shows erosion in the connected pores within the solidified material that attributed to the interaction of CKD alkali metal ions present in the solidified matrix with the chemical constituents present in the aqueous solution. It should be noted that formation of open microstructures and discontinuity of pores will have adverse impact on solidified material properties and its overall durability.

3.3.2. Assessment of the leaching behavior

Leaching tests were used to evaluate the durability performance of SSCKDM. In these tests solidified specimens were kept in contact with different aqueous environments for certain periods of time after which metal ion concentrations in aqueous solution were measured and compared with regulatory standards. Leaching behavior of SSCKDM, CkD, and SSCKDM after inclusion of anti-leaching agent are discussed below.

3.3.2.1. Leaching behavior of SSCKDM. Test results shown in Figs. 11 and 12 indicated that the main leached components are sulfate, Ca, K and Mg and some traces from Al, Cr and Sr suggesting dissolution of fractions from the solidified matrix into aqueous media. It is known that metal ions have lower leachability in alkaline media than acidic ones due to the basic nature of metal oxides.
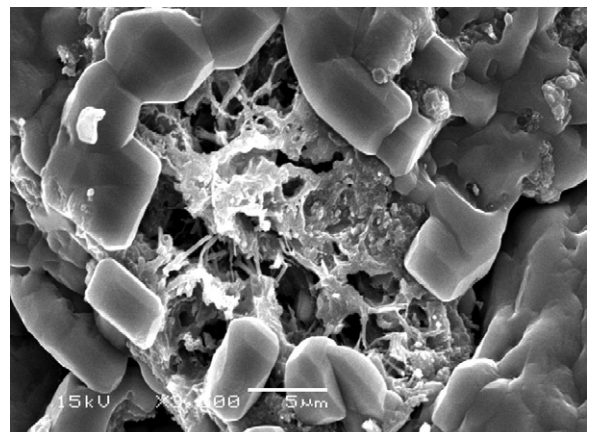

Fig. 9. SEM image of sulfur SCKDM illustrating void formation due to fast cooling.

Fig. 10. SEM image of sulfur SCKDM after immersion in aqueous environment.
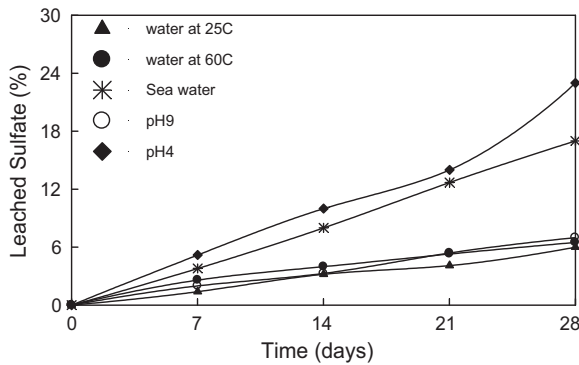
Fig. 11. Variations of sulfates leached from sulfur SCKDM with time in different aqueous environments.

Calcium oxide reacts with water to form alkaline hydroxides while, magnesium oxide does not react with water; but it is basic when it reacts with acid to form salt. It was observed that there are differences in the rate of leached materials in distilled water at 25 and 60 °C. The leached rate of metal oxides was low at room temperature but, slightly enhanced with increased temperature as shown in Figs. 11 and 12. High temperature accelerated the leaching process because solubility of metals depends on temperature and increases as temperature increases [20]. The observed high product of leached alkali metals and sulfates in sea water is due to the interaction between SSCKDM and sea water salts resulting in the formation of water soluble compounds, which are then leached away. The leached metals and sulfates rapidly increase with time throughout the test period.

3.3.2.2. Leaching behavior of CKD. Table 4 summarizes the short- and long-term leaching performance of CKD in distilled water. The results indicated that CKD has very high alkali and sulfate contents. The alkalis exist as alkali sulfates such as arcanite (K_2SO_4), $NaSO_4$ and sylvite (KCl), and an assemblage of oxidized products such as lime. These products are unstable or highly soluble at earth surface conditions [21]. When CKD contacts water these products will either dissolve completely or the less soluble secondary phases will be precipitated. Therefore, the concentration of some constituent elements in CKD leachate will be controlled by the solubility of the secondary precipitates while, the concentration of others will be controlled by their availability to the leachate solutions and by their diffusive fluctuation into the solution from the leaching of primary phases over time. To differentiate between these two classes of elemental behavior, Reardon et al. [22] recommended conducting leaching tests on a particular waste at least at two different solid/water ratios. Then, if an element's concentration does

not double when solid/water ratio is halved, there must be a solid phase control on its concentration in solution. Experimental test results show that the concentrations of leached Ca, Na and K were very high due to high solubility of the bearing minerals (halite and sylvite). The release of other elements (Sr and Cr) was found in lesser amounts.

3.3.2.3. Inclusion of anti leaching agent. Additions of anhydrous sodium sulfide ranging from 1 to 10 wt% to the solidified matrix were investigated. Since the optimal quantity of anhydrous sodium sulfide required depends on the concentration of metal ions present in the waste it was observed that the preferred amounts ranged between 4 and 6 wt%. Addition of anhydrous sodium sulfide as anti-leaching agent resulted in reduction of the leached heavy metals, without lessening of the leached alkali metals and anion from the SSCKDM.

Colombo et al. [23] and Lin et al. [24] reported that the use of anhydrous sodium sulfide as an anti-leaching agent will immobilize metal ions through chemical bonding hence, preventing metal ions from escaping into the environment. However, the newly formed products remained chemically available to react with metal ions even when it is immobilized in the waste matrix. It should be noted that as long as no moisture permeates the waste form, the anti-leaching agent and available metal ions in the waste matrix remain un-reacted. However, when moisture permeates the waste matrix metal ions form precipitates.

3.3.3. Leaching mechanism

A solidified waste is a porous solid matrix which is partially saturated with water. The pore water in the solid matrix is in chemical equilibrium with the solid phase. When the solid matrix is exposed to leaching conditions, the equilibrium is disturbed. The resulting difference in chemical potential between the solid and the leachate solution causes a mass flux between the solid surface and the leachate. This in turn causes concentration gradients that result in bulk diffusion through the solid matrix [25,26]. Transport can either be by diffusion of metal ions from the solid matrix surface into the bulk aqueous phase, or by dissolution into the water in matrix pores. Consequently, the porosity and integrity of the waste form is of major concern.

Leaching will take place when the chemical constituents in the solid matrix pore fluid exist in ionic form. The amount of dissolution which occurs is dependent on the solubility of the constituent and the chemical makeup of the pore water, particularly its pH. Under neutral pH leaching conditions, the leaching rate is controlled by molecular diffusion of the soluble species. Under acid conditions, however, the rate will also be governed by the rate of penetration of the hydrogen ions into the solidified matrix, since this establishes the speciation and solubility of the pollutants present.
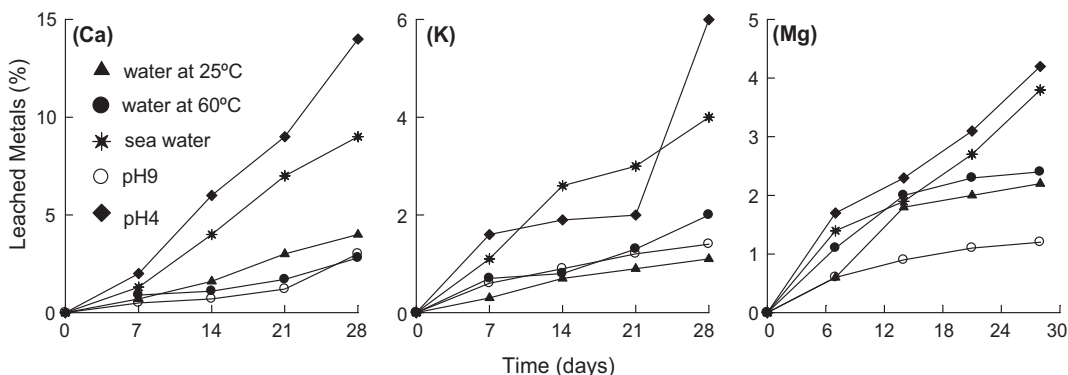

Fig. 12. Variations of the amount of Ca, K and Mg leached from sulfur SCKDM with time in different aqueous environments.

Table 4
Leached metal ions and anions form CKD (mg/kg).

Leaching test	Time (h)	Water/CKD	Alkali metals			Heavy metals		Anions	
			Ca	K	Na	Sr	Cr	SO$_4$	Cl
Short-term	6	2 L/kg	1418	2093	226	7.5	17	1737	1286
Long-term	18	8 L/kg	1399	701	78.8	11.8	11	576	376

Acid attacks CKD-based paste through permeation of pore structure and ion dissolution. Acid consumes most of the calcium hydroxide in the leachate layer and leaves a highly porous structure. Experimental results have shown that the thickness of the leachate layer is usually less than 10 μm [27]. Diffusion across this layer can be considered a steady state process since the leachate provides little resistance to diffusion. At the leaching front, diffusion of hydrogen ions proceeds as if the porous medium in infinite and dissolution reactions occurs in the pores. Proton transfer reactions are usually very fast, with half-lives of less than milliseconds. Hence, dissolution reactions can be treated as diffusion-controlled fast reactions. The whole process than can be described as steady state diffusion across the leachate layer, and unsteady state diffusion-controlled fast reactions in the porous leaching front [28].

3.3.4. Leachate transport modeling

Once metal ions become soluble, they are transported from the solid matrix through the leached zone to the leaching solution by molecular diffusion. The flux of the constituent within the solid can be described by Fick's first law as:
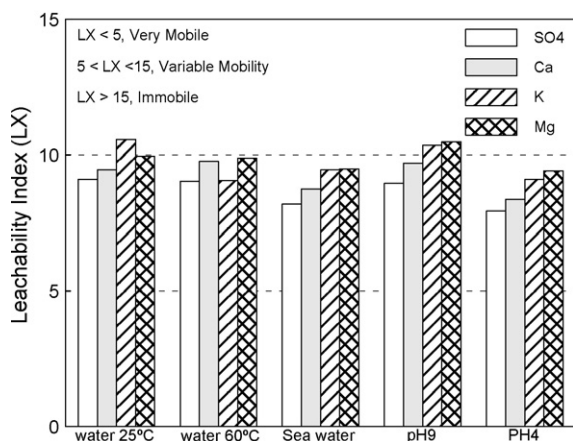
$$J_c = -D_o \frac{\partial c}{\partial x} \tag{1}$$

where J_c is the flux, c is the concentration of constituent, D_o is molecular diffusion and x is distance.

A semi-infinite medium diffusion model with uniform initial concentration and zero surface concentration can be used to interpret the kinetic data generated from batch leaching tests [29]. The equation takes the form:

$$\left[\frac{\sum_{i=1}^{n} c_i}{c_o} \right] \left[\frac{V}{S} \right] = 2\sqrt{\left[\frac{D_e}{\pi} \right]} \sqrt{t_n} \tag{2}$$

where c_i is pollutant loss during leaching period (mg), c_o is initial amount of pollutant in specimen (mg), V is volume of specimen (cm^3), S is surface area of specimen (cm^2), and D_e is effective diffusion coefficient (cm^2/s).

For evaluation solidified waste forms, the leachability index as described by Eq. (3) is recommended as a standard method [24]:

$$LX = \log \left[\frac{\beta}{D_e} \right] \tag{3}$$

where LX is leachability index (dimensionless), β is a constant with an assigned value of 1 cm^2/s.

The leachability index is used to compare the relative mobility of pollutants on a uniform scale which varies from very mobile for values of 5 ($D_e = 10^{-5}$ cm^2/s) to immobile for values 15 ($D_e = 10^{-15}$ cm^2/s) or greater [29]. The calculated results shown in Fig. 13 indicate that the mobility of SO$_4^-$, Ca, K, and Mg from the solid matrix tested in acidic (pH4), neutral (water with different temperatures), and alkaline (pH9) media can be classified as medium.

4. Conclusion

In this study, alkaline solid waste material (cement Kiln dust, CKD) has been evaluated for its potential use as viable aggregate material in the production of sulfur polymer concrete. The behavior of manufactured sulfur solidified cement kiln dust material (SSCKDM) was studied through various conditions such as mix design, curing conditions, amount of sulfur binder, sulfur binder to aggregate ratios and filler percentage. SSCKDM specimens were subjected to various tests under hydrated condition to verify the stability of the manufactured product towards harsh environments. The results showed a significant reduction in the strength of SSCKDM compared to control samples. This reduction in strength can be attributed to the chemical composition of CKD; the tested CKD was characterized by its high alkali, sulfate contents, and the presence of oxides such as lime which is unstable and highly soluble.

Durability of SSCKDM was improved by the addition of 0.35% glass fiber, which increased the strength and controlled crack formation. The potential addition of anhydrous sodium sulfide as anti-leaching agent resulted in reduction of the leached heavy metals, without decreasing of the leached alkali metals and anions from the SSCKDM. The leaching rate of metal and heavy metal ions from SSCKDM increased and the mobility of these leached species in different environments were classified as medium based on the leachability index method of calculation. It is concluded that the use of CKD waste material as is as an aggregate material in the production of sulfur polymer concrete is not recommended because of its physical and chemical instabilities when subjected to harsh environmental conditions.

Fig. 13. Leachability indices of SO$_4^-$, Ca, K and Mg leached from sulfur SCKDM with time in different aqueous environments.

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