RECOVERY OF POTASSIUM SALTS FROM KILN DUST OF LOCAL CEMENT PLANTS

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ABSTRACT

Enriched levels of soluble potassium sulfates in alkali rich cement kiln dust (CKD) makes such dust a promising raw material for the extraction of potash or its soluble salts. This study was carried out to investigate leaching of potassium salts from CKD produced in a local cement plant using water, and 20 wt.% calcium nitrate solution as leachants. Leach tests at several liquid/solid weight ratios, different reaction temperatures, and times revealed that 78.7 % of potash could be extracted using water at a 5:1 liquid/solid weight ratio, upon leaching for 15 minutes at 70 ^{o}C. Similar tests carried out using 20 wt. % calcium nitrate solutions revealed that 96.1 % of potash could be extracted upon 45 minutes of leaching at these same liquid/solid weight ratio and temperature. Furthermore, the large reduction in the alkali content of CKD upon such treatment makes this material suitable to recycle as a kiln feed, as well.

Keywords: *cement kiln dust, potash extraction, water leaching of CKD, calcium nitrate leaching of CKD*

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1. INTRODUCTION

Hundred thousands of tons of cement-kiln dust (CKD) are generated annually from cement plants in the Kingdom of Saudi Arabia. The bulk of this dust, mostly with high alkali contents, is land filled with a significant financial loss to the local cement industry in terms of the value of raw materials, processing, and energy consumption during pyroprocessing, dust collection, and disposal. This fine dust, which emits from cement kilns, is not totally recycled to prevent the build up of excessive salts in the cement product. The alkali salts in the dust are derived from the clay raw materials, which include potassium and sodium feldspars. CKD consists mainly of partially calcined kiln feed, and as such, is generally suitable for recycling to the kiln. However, continuous recycling of CKD to the kiln can soon offset the equilibrium between the alkali levels in the kiln feed and the internal cycle of volatilization and condensation within the kiln, resulting in high alkali clinker. This, of course, is not suitable for plants intending to make low alkali cements that meet the national Saudi requirement of low alkali cement, which specifies a limit of 0.6% equivalent of Na_2O for contained alkali. The alkali content must be kept low to prevent concrete from decrepitating, which might result from a reaction between the alkali and silica in some reactive aggregates in concrete.

Various methods for utilizing CKD in industrial applications, including existing or proposed methods for alkali removal, are reported in the literature. Bhatty (1995) provides a general review of these methods. Because of the generally high lime content of CKD and subsequent ability to harden upon exposure to moisture, CKD has been used as a binder in soil stabilization suitable for a sub-base in streets and high way construction. It is commonly used as a mixture with different solid- waste materials such as waste glass, fly ash, and wastewater sludge with the addition of cement or other admixtures if necessary (Nicholson, 1978; Sayah, 1993; Miller et. al., 1980, and Bhatty, 1983)

A great deal of work has been done on the use of CKD in blended cements. Most published work report a loss in strength, setting time, and workability due to the presence of high alkalis in the dust. It is also been reported that addition of fly ash to these blends tends to improve these properties and reduce the potential problems from alkali-silica reaction (Daous, 2000; Klemm, 1993; Bhatty, 1984; Daugherty and Funnel, 1983, Wills, 1983).

CKD has been used as a substitute for lime in stabilizing wastewater streams. This is possible primarily because of the high neutralizing potential of the CKD (high $CaCO_3$ and CaO) and fine particle size distribution having Blaine finenesses often greater than 800-m2/ kg. Up to 35% addition of CKD has satisfactorily met the specified pathogen control level in sewage sludge. High PH, an exothermic reaction, and the resulting accelerated drying when CKD was added were the factors mainly responsible for the pasteurizing effects on municipal wastewater sludge (Nicholson, and Burnham, 1988; Burnham, 1987).

Other methods reported in the literature suggest the use of CKD directly as a fertilizer material because of its high lime content (for acid neutralizing capacity) and its high

potassium concentrations (Risser et. al., 1981; Baker et. al., 1975; Preston, 1993). Other miscellaneous methods include the use of CKD as a partial replacement for soda in the production of glass where color and high chemical stability are not essential (Fraiman et. al., 1991), as a decolorizing agent in the clarification and purification of sugar solutions (Klemm, 1980), in stabilizing soils contaminated with polychlorinated biphenyls (PCBs) (Einhaus, et. al., 1991), as an absorbent for cleaning up spills in garages and roads (McCants, 1952), and as an additive to remove undesirable elements from leachates produced in water leaching of fly ash (Duchesne and Reardon, 1999).

Enriched levels of soluble alkalis (i.e., K_2SO_4) in CKD make it a promising raw material for the extraction of K_2O or its soluble salts. A number of patents have been issued on the subject, most of which utilize aqueous dissolution of soluble potassium salts that are later removed as a saleable commodity and the water recovered for reuse. The potassium-free dust is usually recycled as kiln feed.

Dean (1972) recovered a substantial amount of alkali salts from CKD by mixing it with H_2O in successive stages at temperatures between 21 and 99 ^{o}C. The supersaturated solution thus produced was cooled and alkali salts crystallized and separated. Singleton and Bruce (1975) treated the dust with fresh water at elevated temperatures to essentially dissolve alkali chlorides and sulfates and subsequently remove them by crystallization. The remaining solution is carbonated to form calcium carbonates for recycling

McCord (1977) recovered the alkalis by leaching the kiln dust at higher temperatures with an aqueous solution of KCl. The extract is cooled for crystallization of KCl and removed. The washed CKD is reclaimed for use as kiln feed. Klemm (1980) proposed the separation of alkalis as K_2SO_4 from the high alkali-dust (~ 13 % K_2O) for agricultural purposes. The K_2SO_4 was extracted by mixing CKD with hot water followed by filtering, cooling the aqueous brine, and K_2SO_4 crystallization. The remaining material can then be used as a raw feed substitute. A yield of more than 86 % was reported by lowering the PH with carbon dioxide, thus preventing the formation of the double salt of K, and Ca sulfates known as syngenite.

Wolfe (1992) reported on leaching tests to remove alkalis from fresh CKD and CKD stockpiled over the years. Tests on the stockpiled CKD showed that more than 80 % alkali (K_2O) was removable by using ordinary tap water with or without additives at ambient temperature. Almost 100 % more alkali was removed from stockpiled CKD than from fresh CKD.

Another approach, proposed by Wilson and Anable (1986), is the removal of alkalis by pyrotreatment of palletized dust. Here the K_2O is volatilized in the presence of SO_3 by heating the dust above 1300 ^{o}C in a reducing environment generated by coal addition. The resulting low-alkali residues were tested as Portland cement, which exhibited strength greater than ASTM standards.

Earlier, Klemm (1980) reported that high-alkali kiln dust could be fused to separate K_2SO_4 as liquid. Several operational difficulties were cited, however. First, although K_2SO_4 in the dust has a melting point of 920 ^oC, the dust itself had to be melted beyond 1400 ^oC to volatilize K_2SO_4 and need to be separated from the fused dust. Second, the K_2SO_4 is reactive and fuses with ceramics, and third, the K_2SO_4 fumes tend to react with the furnace heating elements and eventually inhibit their proper functioning.

The chemical, mineralogical, and physical compositions of CKD varies from one plant to another. These depend on raw material, type of kiln operation, dust collection method, and type of fuel used in the plant (Klemm, 1993).

The objective of this study was to investigate leaching cement kiln dust, produced in local Saudi cement plants, using water or an aqueous solution of calcium nitrate as leachants to produce potassium or potassium-nitrogen fertilizers. In this communication, the results of a series of CKD leaching experiments conducted at three liquid/solid weight ratios, four different leaching temperatures, and several leaching times are presented. The data are used to examine the effects of these important parameters on the leaching process and to determine the most suitable conditions for aqueous leaching of CKD and leaching with aqueous solution of calcium nitrate. This study constitutes an important step towards the utilization and treatment of large quantities of waste CKD produced annually in the country to make it suitable to recycle as a kiln feed, and thus alleviate a standing disposal and environmental problem, and produce value added products in the process.

2. MATERIALS AND METHODS

2.1 Materials

The cement kiln dust used in this study was obtained from the Arabian Cement Company Ltd. in Rabigh, Saudi Arabia. The sample, which was rich in calcium, and alkalis, represents dry materials collected from the electrostatic precipitators above the rotary kiln. The chemical analysis of CKD and the corresponding analysis of Portland cement produced by the same company are given in table (1). The CKD had a solid density of 3.08 g/cm^3, a bulk density of 1.17 g/cm^3, and a porosity of 0.62. The calcium nitrate used in this study was BDH Analytical Reagent-Grade $Ca(NO_3).4\ H_2O$.

2.2 Experimental

For each of the leachants (distilled water, and 20 wt% calcium nitrate solution) used in this study, a series of batch leaching experiments were performed by reacting samples of CKD at 3:1, 5:1, and 10:1 liquid: solid weight ratios for different periods of time ranging from 5 to 60 minutes, and at four reaction temperatures of 30, 50, 70, and 80 ^oC. All experiments were carried out in 250 ml glass conical flasks placed in a thermostatically controlled horizontal shaking bath maintained within 0.5 ^oC of the set temperature.

The necessary number of replicate samples for each liquid:solid mix was reacted to provide the required solution samples for each reaction period and reaction temperature employed in the study.

In each leaching experiment, the required amount of the used leachant was first added to the conical flask, which was then placed in the shaking temperature-bath set at the desired temperature, and was allowed to thermally equilibrate. The required weighed amount of CKD was then gradually added to the leachant while maintaining continuous shaking of the solution in the flask. The reaction was timed from the instant all the required amount of CKD has been added. At the end of the specified reaction period for each sample, the slurry was filtered through a .22-μm paper filter, and washed five times with 20 ml portions of distilled water. The resulting filtrate of each sample was then analyzed for leached potassium ions using Solar M5 Atomic Absorption Spectrophotometer (Thermo Elements, 2001).

3. RESULTS AND DISCUSSION

The percent of potassium released from CKD with leaching time in water/CKD leachates at different leaching temperatures is shown in Figs. (1-4). The leaching behavior of this element shows that a large percentage of the total mass of potassium present in CKD is released upon addition of water. Beyond the first 15 minutes of leaching, there is generally no change in potassium concentration with reaction time. This observation indicates that this element is originally present in CKD as readily soluble salts.

These data also show the release of K in Leachate solution increases with an increase in the liquid/solid weight ratio, and with leaching temperature. However, beyond the initial 15 minutes of leaching, the increase in K released in these water/CKD leachates diminishes beyond a 5:1 liquid/solid weight ratio and 70 $^{\circ}$C. This is further illustrated in Fig. 9, which shows the percent of K released versus leaching temperature at different liquid/solid weight ratios after the initial 15 minutes of leaching.

Although these figures show high percentage of K released for most runs, the percentage released for the 3:1 runs is significantly lower at all leaching temperatures employed in this study. This indicates the existence of a solubility control on K concentration at very low water/CKD ratios.

The results for the leaching experiments of CKD with 20 wt.% calcium nitrate solutions are shown in similar plots in Figs. (5-8). These data show similar characteristic leaching behavior of potassium with a calcium nitrate solution to that with water. However, for any given reaction time, the percent of K released using calcium nitrate solution is always larger than that obtained with water at similar leaching conditions of liquid/solid weight ratio, and leaching temperature. On the other hand, the reaction time needed to reach equilibrium concentration of K in leachates of all experiments carried with calcium nitrate solution is approximately 45 minutes, compared to the 15 minutes observed in leaching experiments employing water.

Similar solubility control on potassium concentration is observed in calcium nitrate solution leaching-experiments run at 3:1 liquid/solid weight ratio as that observed in leaching experiments employing water.

These data further show that, beyond the initial 45 minutes of leaching, no further increase in K released in the calcium nitrate solution/CKD leachates is observed beyond that obtained with experiments carried at 5:1 liquid/solid weight ratio, and 70 $^{\circ}$C. This is further illustrated in Fig. 10, which shows a plot of percent of K released versus leaching temperature at different liquid/solid weight ratios.

The increase in potassium release from CKD when using calcium nitrate solution over that when using water as leachants could be plausibly attributed to the higher solubilizing effect of nitrate ion, in one hand, and to equilibrium considerations, on the other, resulting from the possible reaction between potassium sulfate present in CKD and calcium nitrate solution to give potassium nitrate and the much less soluble calcium sulfate salt. The formation of such less soluble calcium salt is expected to shift the equilibrium in the direction to increase the solubility of potassium sulfate in CKD.

4. CONCLUSIONS

Samples of cement kiln dust were leached with water, and 20 wt.% calcium nitrate solution at three different liquid/solid weight ratios, and four different temperatures for varying leaching periods as a first step towards characterizing `the leaching behavior of potassium salts from alkali rich CKD with these two leachants. The following conclusions were made:

- CKD leach tests conducted with water, and calcium nitrate solution at different liquid/solid ratios and different temperatures provide evidence that there is no solubility control for the concentration of potassium in solutions of leaching experiments carried out at 5:1 or higher liquid/solid ratios and 70 $^{\circ}$C or higher. Under these leaching conditions, potassium equilibrium concentration in solution is reached at in approximately 15 minutes in leaching with water, and 45 minutes in leaching with calcium nitrate solution.

- Utilizing the leaching conditions cited above, it is possible to extract at least 78.7 % of the potassium present in CKD with water, and 96.1 % of this element with 20 wt.% calcium nitrate solution.

- It is technically feasible to extract potassium from waste CKD by leaching with water or calcium nitrate solutions, however, further studies are needed to investigate the compositions of the potassium salts present in these leachates, and the crystallization of these salts, and their mineral compositions to produce potash or nitrogen – potash fertilizers.

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Table 1. Analysis of Portland cement and CKD, weight percent

Constituent	Portland Cement	CKD
CaO	63.77	42.02
SiO_2	20.36	14.42
Al_2O_3	5.33	4.14
Fe_2O_3	3.97	2.61
MgO	2.10	1.55
K_2O	0.14	7.2
Na_2O	0.48	2.60
SO3	2.72	4.21
Cl^{-1}	0.03	4.12
L.O.I	--	12.00
Insoluble Residues	--	5.13

Fig.(1) Percent of K released in the water/CKD leachates at 30 ºC and different liquid:solid weight ratios.
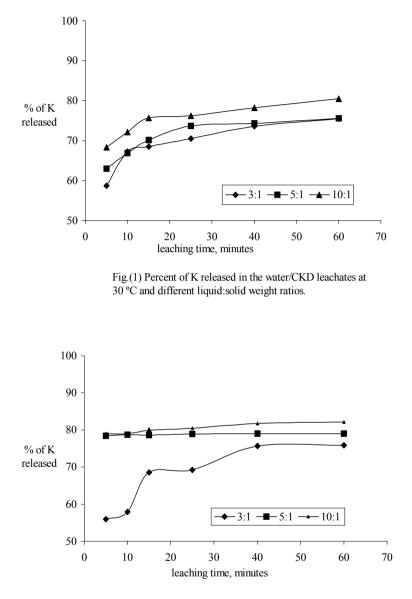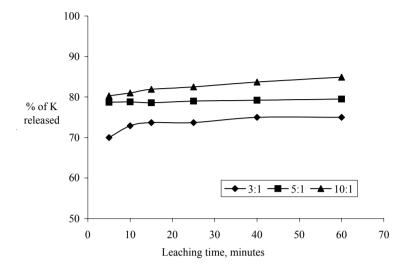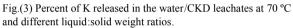
Fig. (2) Percent of K released in the water/CKD leachates at 50 ºC and different liquid:solid weight ratios.

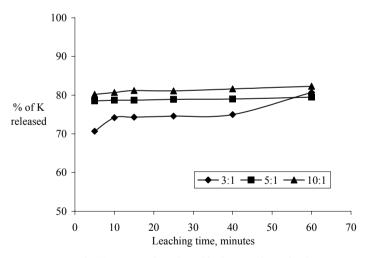Fig.(3) Percent of K released in the water/CKD leachates at 70 ºC
and different liquid:solid weight ratios.

Fig.(4) Percent of K released in the water/CKD leachates at 80 ºC
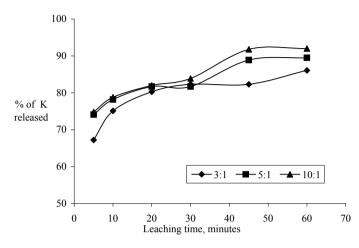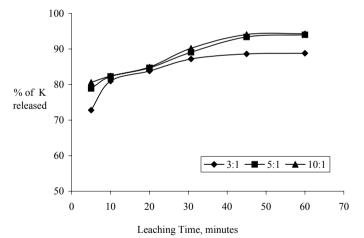and different liquid:solid weight ratios.

Fig.(5): Percentage of K released in calcium nitrate solution/CKD leachates at 30 ºC and different liquid:solid weight ratios.
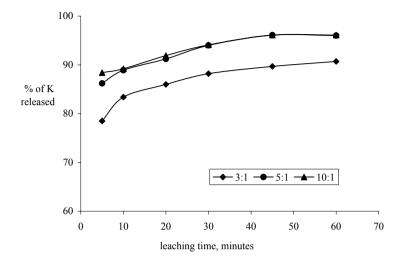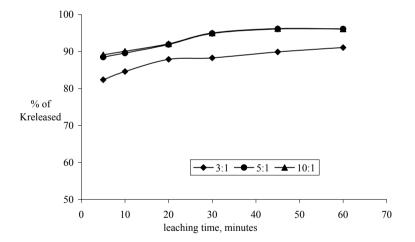

Leaching Time, minutes

Fig.(6): Percentage of K released in calcium nitrate solution/CKD leachates at 50 ºC and different liquid:solid weight ratios.

Fig.(7): Percentage of K released in calcium nitrate solution/CKD leachates at 70 ºC and different liquid : solid weight ratios.

Fig.(8): Percentage of K released in calcium nitrate solution/CKD leachates at 80 ºC and different liquid : solid weight ratios.
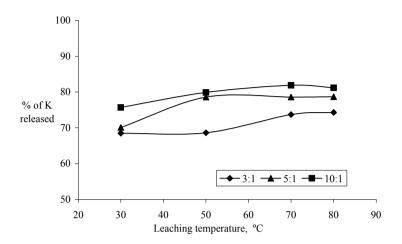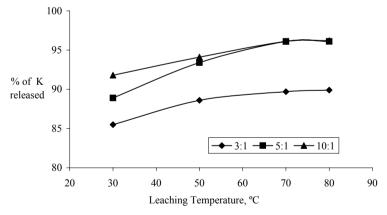
Fig (9):Percent of Potassium released in the water/CKD leachates
after the initial 15 minutes of leaching at different temperatures and
liquid : solid weight ratios.

Fig(10):Percentage of Potassium released in the Calcium Nitrate
solution/CKD leachates after the initial 45 minutes of leaching at
different temperatures and liquid : solid weight ratios.