Original
Received December 7, 2001
Accepted for Publication February 15, 2002
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Acid Gas Sorbent Prepared from Solid Wastes Containing Calcium-based Compounds

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For applying calcium-based (Ca-based) solid wastes to renewable source of calcium derived products, different calcium-based solid wastes from coal burnt ash, coal slag and iron slag were tested for dry sorption of HCl. The sorption capacities of Ca-based wastes for HCl were related to the soluble alkali amount involved, as well as specific surface area of the solid. Coal burnt ash and slag treated by hot water and alkali curing were found to be greatly improved in HCl sorption capacity, almost equivalent to that obtained by the use of conventional calcium oxide or calcium hydroxide.

Key Words : acid gas sorbent, coal burnt ash, dechlorination, slag, solid waste

1 INTRODUCTION

To facilitate compatibility between sustainable economic development and environmental protection, legislation on waste recycling and management has been enforced. It becomes therefore important for an environment-friendly society to design and manufacture industrial products appropriately, so that they can be easily recycled to minimize waste generation.

The present paper describes reutilization of calcium-based (Ca-based) solid wastes which have been mainly discharged and landfilled in Japan. A cascade recycling system is characterized by a complementary recycling system, in which individual wastes are successively recycled from the upper stream to the downstream of the process, in accordance with the change in their adaptability as material resources. As these solid wastes, in general, involve alkaline or metal-based compounds, it is expected that they might be reused as raw materials for environmental materials such as absorbents and new functional materials [1-18]. In general, it is possible to use calcium compounds contained in Ca-based solid waste for HCl sorption. Some research works on HCl sorption have been conducted by using zeolites and compounds which are Ca-based or Na-based [19, 20]. Improvement of these gas sorbents for HCl sorption has also been done by applying various activation methods [21]. In the present work, an attempt is made to reutilize Ca-based solid wastes as acid gas sorbents, before eventually being returned to a downstream process of cement production. Coal burnt ash and blast furnace slag which are discharged as Ca-based solid wastes were particularly treated with hydration and curing, so that they might be applied to HCl sorbent with high efficiency.

2 APPLICATION OF CASCADE RECYCLING TO Ca-BASED SOLID WASTES REUTILIZATION

2.1 Cascade Recycling of Solid Wastes

Raw materials are characterized by having low entropy values, which is a measure to evaluate its potential use as raw material relevant to the manufacturing process concerned. As illustrated in Figure 1, the entropy of a raw material increases as it is used and then discharged as waste. In cascade recycling, the waste discharged from an upper stream process is recovered and reused as raw material for a downstream process. A waste material discharged from the process is usually contaminated physically or chemically with undesirable substances. In general, once converted to a heterogeneous state, it is difficult to recover virgin raw material from such wastes. However, if the contaminated raw material still preserves its proper function to some extent, it can be

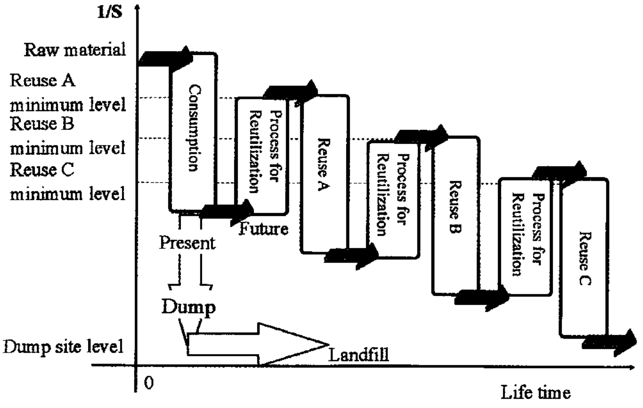


Figure 1 Cascade recycling for reutilization of solid wastes

reused for another purpose with a minimum effort, until it finally comes to an end use.

2.2 Cascade Recycling of Ca-based Solid Wastes

In general, Ca-based solid wastes as burnt ash, slag and sludge, etc. are discharged in heterogeneous form composed of CaO, SiO_2, Al_2O_3, etc. Since those are elements requisite for cement manufacturing, they are usually recycled to cement materials. Among these main components of CaO, SiO_2 and Al_2O_3, the quantity as well as quality of involved CaO is evaluated by alkalinity. As illustrated in figure 2, solid waste with high calcium content is expected to be reused by making effective use of its alkalinity, before being recycled as cement material. On the other hand, solid wastes with high contents of SiO_2 and Al_2O_3 are applicable to cement materials. In this case, CaO bonds SiO_2 and Al_2O_3 chemically, enhancing their value as cement materials. On the basis of CaO-SiO_2-Al_2O_3 phase diagram in Figure 2, it seems possible that solid wastes containing CaO, SiO_2 and Al_2O_3 are consecutively reused (cascade recycling) from acid gas sorbent to cement materials.

For the achievement of recycling of incinerator burnt ash to regenerative cement, New Energy and Industrial Technology Development Organization (NEDO) and Taiheiyo Cement Corp. have recently developed a new recycling of incinerator ash as "Eco-cement" [22].

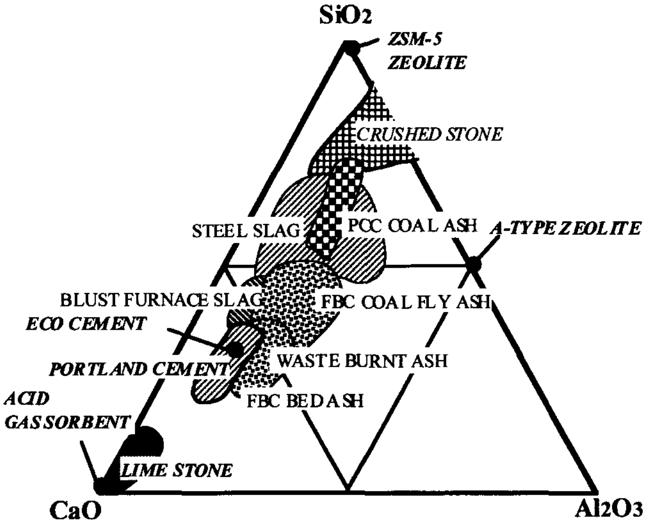


Figure 2 Waste material distribution on CaO-SiO_2-Al_2O_3 phase diagram

Table 1 Chemical composition of Ca-based solid wastes

sample	SiO_2 content [wt%]	Al_2O_3 content [wt%]	CaO content [wt%]	soluble alkali content [ml-1N HClaq. /25g-sample weight]
coal burnt ash				
CFBC(1)	51.2	13.8	26.2	93.02
CFBC(2)	45.7	21.4	23.9	73.06
CFBC(3)	36.3	24.0	26.9	101.15
CFBC(4)	46.1	27.8	12.8	32.19
CFBC(5)	51.6	18.0	20.2	73.76
FBC BF ash	47.2	21.6	6.44	16.93
FBC MC ash	30.8	13.1	17.2	83.08
FBC BM ash	24.3	13.7	33.9	413.37
PC(1)	64.1	28.1	0.87	2.51
PC(2)	59.9	19.1	2.38	10.02
slag				
conveter slag	11.8	2.1	43.4	198.57
blast furnace slag	34.6	13.8	42.3	44.41
electric furnace slag	23.9	9.34	55.5	74.40
paper sludge				
paper sludge(1)	30.0	18.0	22.0	9.52
paper sludge(2)	37.0	27.0	17.0	1.91
shell				
shell waste	0.30	0.54	55.4	6.47
calcium resource				
$CaCO_3$	0.07	0.52	54.2	6
CaO	0.12	0.91	94.8	not measured
$Ca(OH)_2$	0.09	0.70	72.6	630

3 POSSIBILITY OF USING Ca-BASED SOLID WASTES AS ACID GAS SORBENTS

3.1 Criterion for Acid Gas Sorbents

It is considered that Ca-based solid wastes such as coal burnt ash, slag, sludge, etc. differ in physico-chemical properties, since they are formed in heterogeneous state mixed and/or composed of different materials. It is also considered that their properties differ depending on the process and the condition that they experienced. It is therefore significant to provide the information on their fundamental reactivity with acid gas, so that they might be reutilized as acid gas sorbents. As the first step of this study, different solid wastes involving Ca-based compounds were tested to evaluate their HCl sorption capacity. In this study, the HCl sorption capacity is defined as

$$\text{HCl sorption capacity [-]} = \frac{\text{accumulated amount HCl sorbed in 120 min [mol]}}{\text{total accumulated amount HCl flowing through the reactor in 120 min [mol]}}$$

The experiments were carried out with constant space velocity (sample volume: 1.2 mL, total gas flow rate: 300 mL/min, 1000 ppm-HCl). In general, HCl removal is perfomed in flue gas treatment facilities under conventional operation condition of 423-473 K [23]. At this temperature range, our preliminary experimental result showed that CaO had a maximum HCl sorption capacity at 473 K. We evaluate hereafter the HCl sorption performance of Ca-based solid wastes at a constant temperature of 473 K. Table 1 indicates industrial analysis of Ca-based solid wastes employed in the experiment. It is reported that calcium contained in slags is combined with silica phase, to form chemically stable calcium-derived compounds [24]. In view of this fact, the data on HCl sorption capacity is plotted against soluble alkali content. As seen in Figure 3, there is a good linearity between HCl sorption capacity and soluble alkali content. These data are useful to predict HCl sorption capacity of various Ca-based solid wastes.

3.2 Application of Ca-based Solid Wastes to Acid Gas Sorbents

As described above, coal burnt ashes and slags with high soluble alkali content have potential to be applied to acid gas sorbents. Among acid gases, HCl is recognized to be responsible for generation of dioxins. Attention was then focused on effective

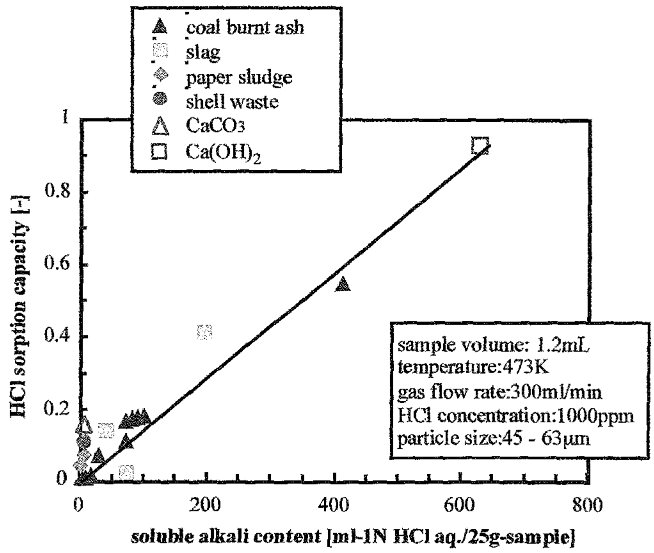


Figure 3 Relation between HCl sorption capacity and soluble alkali content of Ca-based wastes (sample volume: 1.2 mL)

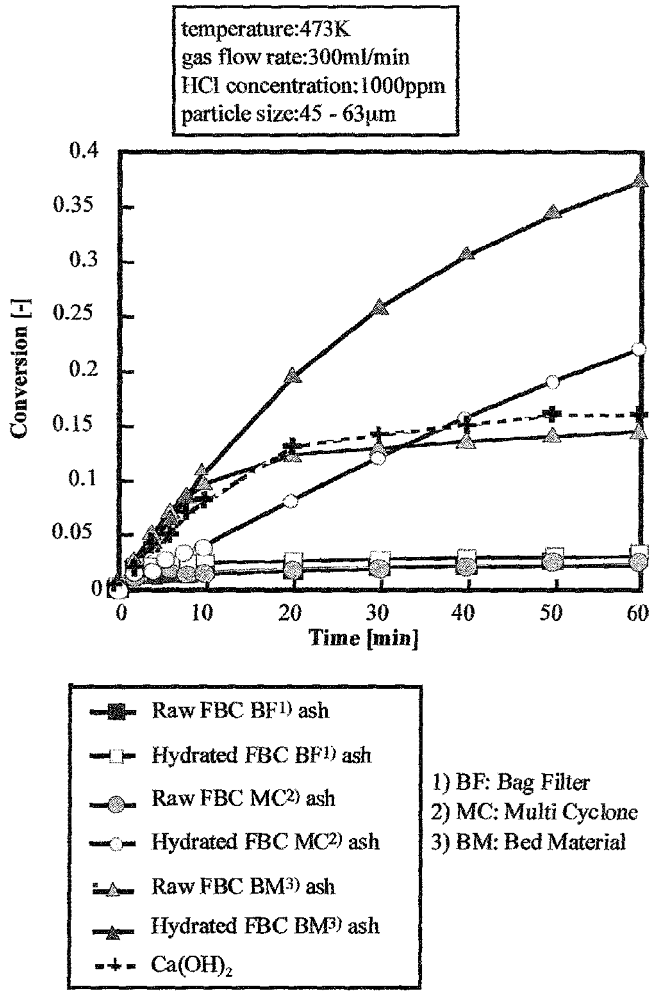
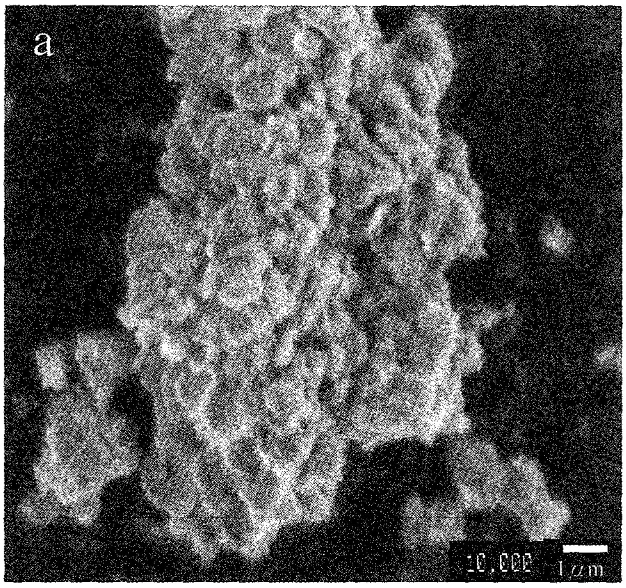


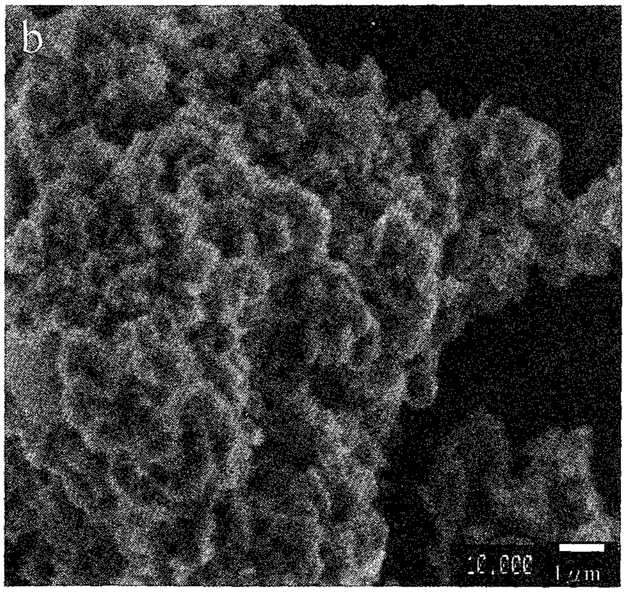
Figure 4 Conversion curves of FBC ash for HCl removal

HCl gas capture by Ca-based dry sorbent in the present work. Fundamental characteristics on sorption of HCl gas by Ca-based solid wastes were studied. In addition, to enhance the efficiencies of these solid wastes for HCl sorption, hydration and alkali curing were applied to coal burnt ashes and slags.

3.2.1 Coal Burnt Ash: Coal burnt ashes discharged from fluidized bed coal combustor (FBC) were employed as test specimen for gas sorbent of HCl, and were subjected to hydration treatment [10,11]. Figure 4 shows the time-conversion curves obtained by the reaction of coal burnt ash with HCl. The



(a) raw FBC BM ash



(b) hydrated FBC BM ash

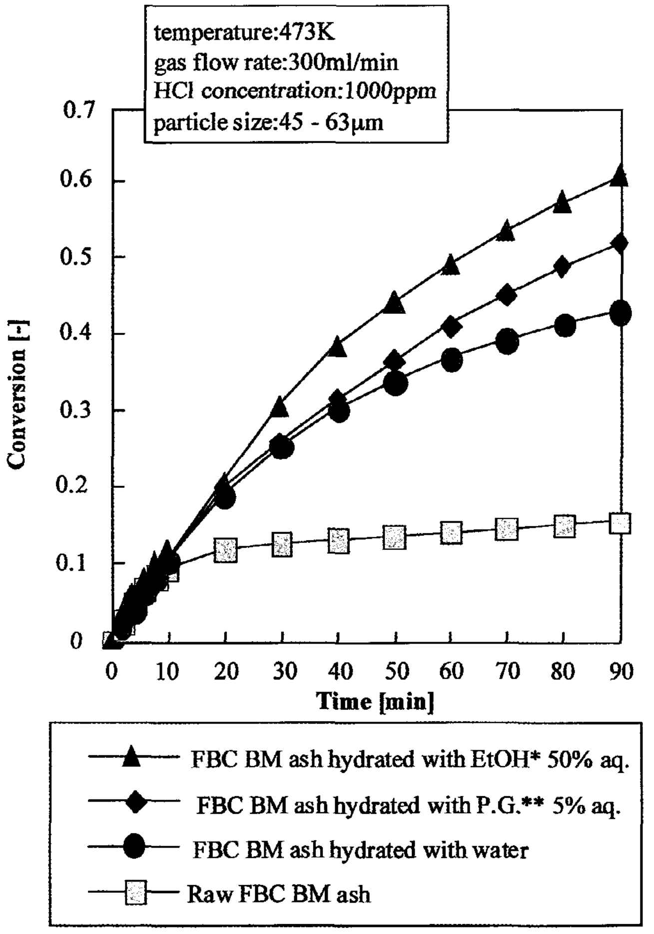
Figure 5 SEM photographs;
(a) raw FBC BM ash; (b) hydrated FBC BM ash

experimental condition was consistent; the reaction temperature was 473 K, and the initial concentration of HCl was 1000 ppm/ N_2-balance, with the particle size of the ash between 44-63 mm. As seen from the figure, all the coal burnt ash used show a similar trend in time-conversion curve. More precisely, coal burnt ash sorbed HCl within a short period (4-20 minutes) from the beginning of reaction. Apparent sorption capacities of three different ashes were 3% for raw FBC BF and MC ashes, and 11% for FBC BM ash, depending on calcium content in the ash. On the other hand, when coal burnt ashes were treated by hydration, HCl sorption capacity was remarkably improved, in particular, for raw FBC MC and BM ashes. HCl sorption capacity of hydrated FBC BM ash was even superior to that of $Ca(OH)_2$ specimen of reagent grade. However, no significant improvement was observed for FBC BF ash, due to inherent low calcium content in the original ash. Figure 5 presents SEM photomicrographs of raw FBC BM ash and hydrated FBC BM ash. It is observed that hydrated FBC BM ash is formed in agglomerated shapes from particulates of submicron sizes; these are assembled into particulates having grain sizes less than 3 mm (Figure 5b). Raw FBC ash shows a similar structure, but discrete grain sizes were less than 1 mm. It is also indicated that adjacent grains were more tightly agglomerated (Figure 5a). The hydration operation seems effective for the growth of $Ca(OH)_2$ crystals.

In Figure 6, HCl sorption capacities of raw FBC BM ash are compared with those treated by water hydration, PG (Polyethylene glycol) hydration, and Et-OH (Ethanol) hydration [25, 26]. It is observed that conversion at 60 minutes of time lapse were increased to 37%, 40% and 46% for water hydration, PG hydration, and Et-OH hydration, respectively. The findings in Figure 6 are explained by pore-surface area distribution data demonstrated in Figure 7. When the raw sample of coal burnt ash is treated with hydration, mezo pores of 1-10 nm in pore diameter developed, which causes 5-10 times increase in the specific surface area. This increase in mezo pores is responsible for the high HCl sorption capacity. In addition to the increase in mezo pores, macro pores of 10-100 nm in pore diameter which is distinctive change for the case of Et-OH hydration, contributed to a higher HCl sorption.

3.2.2 Slag: Slag from an blast furnace was tested for HCl sorption at moderate temperatures around 473 K. In general, calcium component in slag was considered to form chemically stable silica compounds [24]. Alkali treatment with sodium hydroxide was then applied to blast furnace slag, in order to change its solid structure to improve its HCl sorption capacity.

Figure 8 summarizes the effect of hydration of blast furnace slag on HCl sorption capacity, soluble alkali content and specific surface area [18]. It was found that raw blast furnace slag was greatly improved in its HCl sorption capacity after treatment in NaOH solution. It is seen that soluble alkali content is not so much changed, but specific surface area becomes higher with an increase in treatment time of alkaline solution. Figure 9 shows SEM microstructure of the raw blast furnace slag and the slags treated by alkali hydration, indicating that the surface of raw slag appears smooth, while fibrous structures grow with the progressive alkali treatment. This structural change might bring about a large specific surface area of alkali-treated slags.



** P.G. = Polyethylene Glycol
* EtOH = Ethanol

Figure. 6 Conversion curves of hydrated FBC BM ash for HCl removal

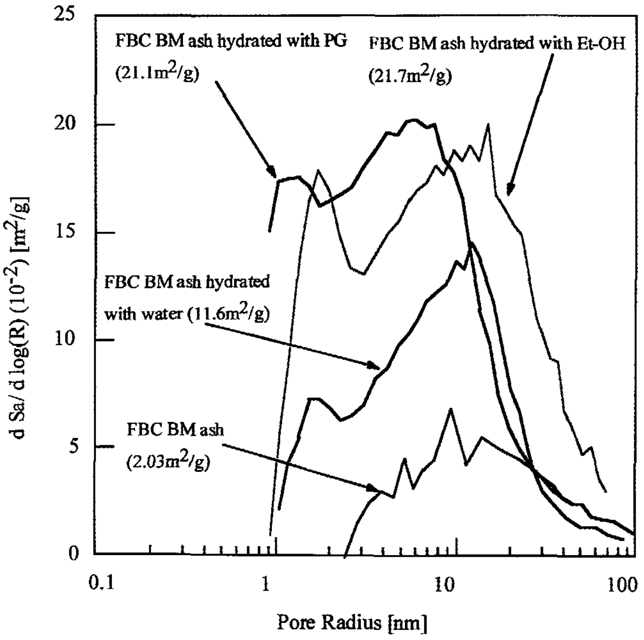


Figure 7 Effect of treatment of raw FBC BM ash

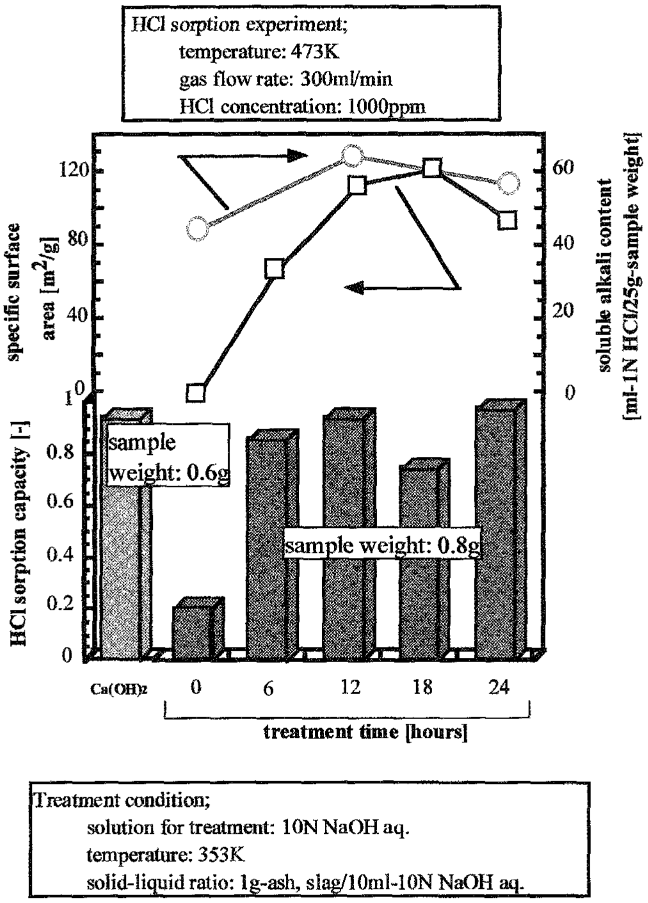
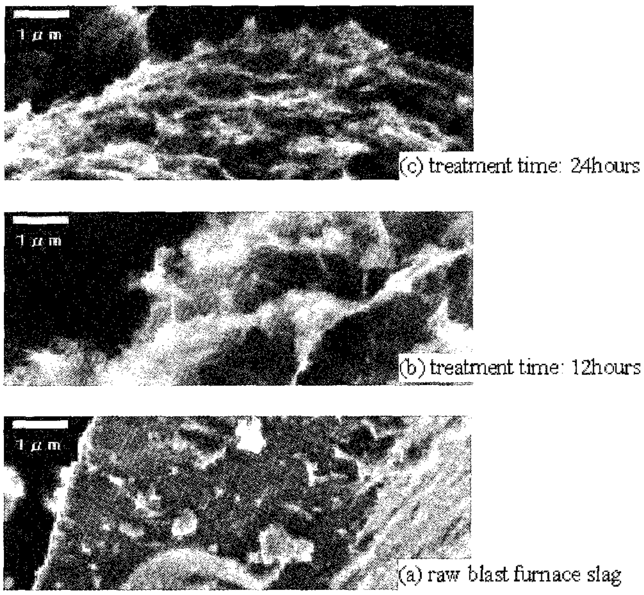


Figure 8 Effect of treatment time on HCl sorption capacity of blast furnace slag



(c) treatment time: 24hours

(b) treatment time: 12hours

(a) raw blast furnace slag

Figure 9 SEM images of blast furnace slag; (a) raw blast furnace slag, (b) treatment time: 12hours, (c) treatment time: 24hours

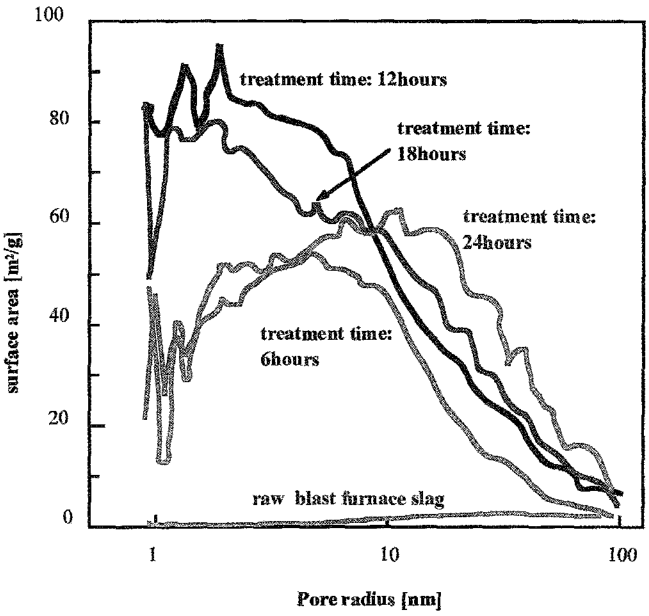


Figure 10 Pore-surface area distribution curves of blast furnace slag

From XRD examination, some kind of zeolites, $(Na_2O)_x$-Al_2O_3-$(SiO_4)_y$-$(H_2O)_z$ and $(CaO)_x$-$(SiO_4)_y$-$(H_2O)_z$ were confirmed. Figure 10 shows the pore surface area distribution curves of blast furnace slag before and after alkali hydration. It is demonstrated that the specific surface area of blast furance slag increases with alkali hydration treatment time. However, it was found that specific surface area after 24 hours of treatment decreased with decreasing in mezo pores (1-10 nm). This decrease in mezo pores may be caused by the change in surface structure in the progress of alkali hydration.

CONCLUSIONS

For applying Ca-based solid wastes to acid gas sorbent, different kinds of coal burnt ash, coal slag and iron slags were tested for dry sorption of HCl gas. It was found that coal burnt ashes showed HCl sorption capacity, depending on the amount of soluble calcium component involved. The employed coal combustion ashes were greatly improved by hydration curing, in terms of their HCl sorption capacity. The improvement of acid gas sorption capacity of treated ash and slag was attributed to physico-chemical structural changes of the treated ash and slag. Ca-based solid wastes were considered to be reused effectively in cascade recycling, before being turned to final end-use of cement materials.

A further development of techniques is needed to apply cascade recycling to proper use for waste management, which results in great decrease in solid wastes.

Acknowledgements- Taiheiyo Cement Corporation is greatly appreciated for providing information on Eco-cement.

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