

Preparation of an efficient humidity indicating silica gel from rice husk ash

J P NAYAK and J BERA*

Department of Ceramic Engineering, National Institute of Technology, Rourkela 769 008, India

MS received 6 May 2009; revised 25 September 2010

Abstract. An efficient humidity indicating silica gel was prepared using rice husk ash as a raw material via sodium silicate extraction and acid neutralization method. Cobalt chloride was impregnated into the silica gel as a colour indicating material. A low concentration of cobalt chloride solution ($0.0005 \text{ mol dm}^{-3}$) was used for the impregnation. The effect of pH of the impregnating solution on the colour development behaviour of the gel was investigated. The specific surface area of the gel was determined by Brunauer–Emmett–Teller method. The gel has been characterized using X-ray diffraction, scanning electron microscopy and visible spectroscopy. The moisture adsorption and desorption kinetics of the desiccant were evaluated using simultaneous thermogravimetry and differential scanning calorimetry.

Keywords. Silica gel; humidity; rice husk ash; cobalt.

1. Introduction

Silica gel desiccant is used to protect sensitive materials from damage due to humidity. Since the gel is normally white or colourless and shows no changes of colour during use, it is difficult to tell when it becomes saturated with moisture and needs to be regenerated or to be replaced. Therefore, a visible indication is necessary to know when the gel is saturated with moisture. Traditionally this has been achieved by impregnating the gel with cobalt salt, usually chloride (Balkose *et al* 1998), which imparts a deep blue colour to the dry gel. The colour of the dry gel changes from blue to light pink upon water vapour adsorption. This sharp colour changing property makes it a most popular desiccant for different industrial applications.

The silica gel is normally prepared from commercially available sodium silicate. The sodium silicate is manufactured by smelting quartz sand with sodium carbonate at 1300°C (Iler 1979; Brinker and Scherer 1990). The process is expensive due to its high temperature requirement. On the contrary, sodium silicate can be prepared at much lower temperature by simply boiling the amorphous silica in sodium hydroxide solution. A cheap source of amorphous silica is the rice husk ash (RHA). Thus, RHA is used as an economic raw material for the production of sodium silicate (Lender and Ruiter 1990; Luan and Chou 1990; Krishnarao and Godkhindi 1992; Kamath and Proctor 1998).

RHA is a waste product generated by the energy producing units which uses the husk as a fuel (Kalapathy *et al* 2000). It has also been used by many workers to derive silica (Cunha and Canepa 1986; Conradt *et al* 1992; Real *et al* 1996; Yalcin and Sevinc 2001; Liou 2004; Ahmed and Adam 2007; Goncalves and Bergmann 2007). In the present work, RHA waste material was collected from a local industry and was used to synthesize silica gel via sodium silicate extraction and acid neutralization method.

A sharp colour change in a small humidity range is desired for an efficient indicating gel. The blue colour intensity of the dry gel directly depends on the weight fraction cobalt salt present in it and uniform dispersion of the salt in the gel. The more the homogeneous dispersion of cobalt salt, the lower will be the amount required to obtain the same colour intensity in the gel. Another objective of this work was to use cobalt concentration as minimum as possible for the interest of health and safety of the desiccant application. The effects of gel washing and effect of pH during cobalt impregnation on the colour development behaviour of the gel were investigated. The moisture adsorption capacity and the regeneration characteristic of the desiccant were also investigated.

2. Experimental

RHA was collected from a local rice mill. Sodium hydroxide (Laboratory Grade, Loba, India), hydrochloric acid (Loba, India) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Laboratory Grade, Loba, India) were used for the preparation of indicating silica gel. RHA was thoroughly washed with water before

*Author for correspondence (jbera@rediffmail.com)

use. Typically, 5 g dry ash was boiled in 100 ml 1 M NaOH solution for 1h under reflux condition to dissolve amorphous silica as sodium silicate. The solution was then filtered to separate residue. After cooling to room temperature, the sodium silicate solution was added drop wise into 1 N HCl solution with constant stirring condition. The pH of the final solution was maintained at 5. Within a few minutes, the sol turned into gel. The gel was broken and washed with water for several times to remove sodium and chlorine ions.

The washed hydrogel was then aged in $0.0005 \text{ mol dm}^{-3}$ CoCl_2 aqueous solution at different pH for 6 days. In separate experiments, the gel was aged at pH 2, 4, 6, 8 and 10 respectively. The aged hydrogel was then separated by filtration and dried at 150°C till it attained constant weight. The dry desiccant was then aged in 90% relative humidity (RH) for 1 day and then re-dried at 150°C to get homogeneous distribution of cobalt salt on the surface of the silica gel.

The washed and unwashed gels were characterized by X-ray diffraction (XRD) using PW1830 diffractometer, Philips, Holland. The microstructures of selected specimen were studied by using scanning electron microscope (SEM, JSM-6480LV). Fourier transform infrared (FTIR) data of selected specimen were obtained using Perkin Elmer FTIR spectrophotometer (Spectrum RX-1). The visible spectra of the gel were collected in Perkin Elmer UV-visible spectrophotometer (Lambda 35). The specific surface area of the gel was determined by the Brunauer–Emmett–Teller (BET) method using Autosorb-1, Quantachrome surface area analyzer. The humidity adsorption capacity of the desiccant was measured in 80% RH, 30°C . The dehydration (regeneration) characteristic of the desiccant was evaluated using thermogravimetric analysis and differential scanning calorimetry (TGA/DSC, Netzsch STA 449 C Jupiter) with a $10^\circ\text{C}/\text{min}$ heating rate under N_2 gas.

3. Results and discussion

The colour changing behaviour of CoCl_2 impregnated silica gel depends on many parameters like chemical composition of the gel, concentration of indicating salt, pH of processing condition, drying, relative humidity, etc. Figure 1 shows XRD patterns of different silica gel powder in their dry state. Unwashed gel (figure 1(a)) shows the presence of NaCl and Na_2SiO_3 crystalline phases. Due to their presence, unwashed gel appears translucent and whitish in colour after drying. Figure 1(b) shows the pattern for properly washed gel which is not impregnated with CoCl_2 . The pattern of impregnated gel (figure 1(c)) is very similar to that of un-impregnated gel. Both the materials show typical amorphous silica XRD pattern. There are no peaks of CoCl_2 in the impregnated gel due to its low concentration, i.e. the concentration was below

the detection limit of X-ray powder diffraction measurement.

Figure 2 shows SEM morphology of unwashed and washed gel. The granular morphology of unwashed gel (figure 2(a)) was due to the presence of NaCl on the surface. During drying of the gel, dissolved NaCl comes to the surface along with water and forms granular microstructure. Those granules were absent in washed gel (figure 2(b)).

The colour development behaviour of impregnated silica gel after drying was dependant on the pH of impregnation mixture. Figure 3 shows the colours of different gels at their dry state (top row) and after their humidification (bottom row). The pH shown in the figure, indicates the equilibrium pH of hydrogel plus CoCl_2 solution during aging. All the specimens were aged with same concentration of CoCl_2 solution. The figure shows that the blue colour of dry gel became faint increasingly with the lowering of pH. It also shows that pH 6 gel has most prominent blue to pink colour changing behaviour. The Co(II) has tetrahedral $[\text{CoCl}_4]^{2-}$ complex structure in dry state, which is deep blue in colour. Upon exposure to moisture the structure changes to the octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex, which is pink in colour (Richardson 1993).

pH 2 gel was nearly colourless in both dry and humidified state. This may be due to low adsorption of cobalt on the gel as the isoelectric point of silica is near pH 2. The colour of pH 10 gel was reddish-brown. The ammonium hydroxide was used to raise pH of the impregnation mixture. At higher concentration of ammonia addition, H_2O -ligand of cobalt complex is replaced by

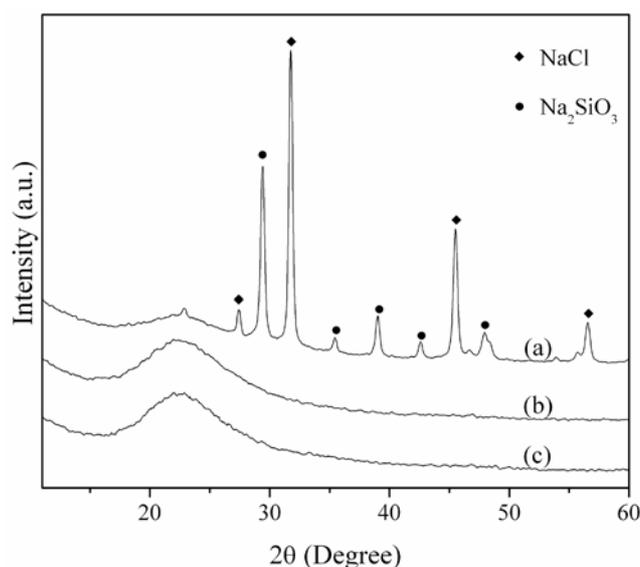


Figure 1. X-ray diffraction patterns for unwashed (a), washed un-impregnated (b) and CoCl_2 impregnated silica gel (c).

in green–yellow region. This green–yellow region absorption was strong in the pH 10 gel and thus it appears reddish-brown in colour.

The moisture adsorption capacity is one of the most important properties of a desiccant. Figure 5(a) shows the water adsorption kinetic of pH 6 gel measured at 80% RH and 30°C. The gel adsorbed about 40% moisture. The BET surface area of the dry gel was 580 m² g⁻¹. The high absorption capacity of the gel was due to its high surface area. The result indicates that the preparation method was efficient to produce a high specific surface area silica desiccant with good moisture absorption capacity.

One reason of high surface area gel formation may be the use of very low concentration of the cobalt chloride. It has been reported (Balkose *et al* 1998) that the pores of silica gel may be filled by the CoCl₂ to some extent depending upon its concentration. The filling of pores lowers the adsorption capacity of the gel. Higher the concentration of CoCl₂, greater the amount of pore filling.

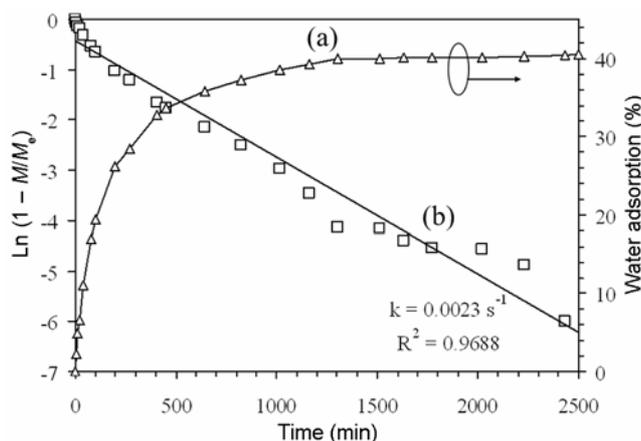


Figure 5. Adsorption kinetic curve (a) and linear dependence of $\ln(1 - M_t/M_e)$ with time (b), for water vapour adsorption on gel (pH 6 specimen) in 80% RH and 30°C.

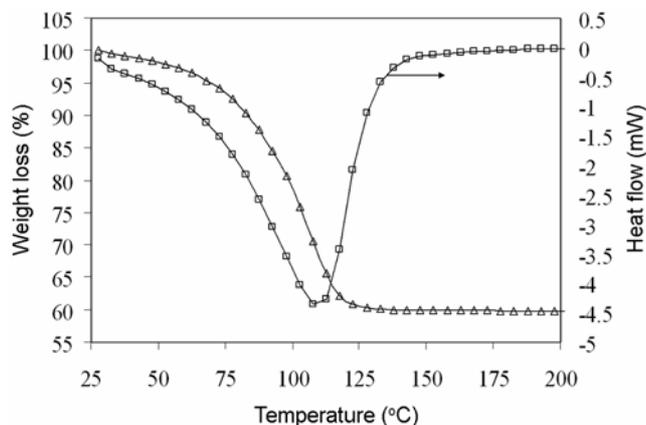


Figure 6. TG/DSC curves of silica gel (pH 6 specimen) after complete humidification.

The other reason may be the use of hydrogel for impregnation. The dispersion of cobalt chloride was uniform in hydrogel and thus a low concentration of salt was sufficient to impart blue colour in dry gel.

The kinetics of water vapour adsorption (figure 5(a)) shows the moisture sorption rate to be high during the initial stages and then gradually becoming low. This phenomenon can be analyzed using linear driving force (LDF) model (Zhong and Yang 1999; Cossarutto *et al* 2001). The model can be expressed as:

$$1 - (M_t/M_e) = e^{-kt}, \quad (2)$$

where M_t is the uptake at time t , M_e the equilibrium uptake and k the rate constant. Figure 5(b) shows that the plot of $\ln(1 - M_t/M_e)$ vs time is linear with the slope (0.0023) equal to the rate constant (k). The results again confirmed that the LDF model is suitable for the description of water vapour adsorption on the silica gel (Li *et al* 2007).

The desiccants are normally regenerated by heating. The regeneration characteristic of humidified gel (pH 6 specimen) was studied using TG/DSC. Figure 6 shows the moisture desorption kinetics of the gel. The desorption starts from about 40°C with a slow rate and with an increased rate from about 75°C. The maximum rate of desorption was at 107°C as shown by DSC endothermic peak. The moisture desorption completes by 130°C. About 40% weight loss was shown by the specimen with a heat of vapourization of about 940 J g⁻¹.

4. Conclusions

The humidity indicating silica desiccant was successfully prepared using rice husk ash waste material as a source for silica. The silica gel was prepared by acid neutralization of sodium silicate solution which was extracted from the ash through sodium hydroxide leaching. The silica hydrogel was impregnated with cobalt chloride solution of 0.0005 mol dm⁻³ concentration at pH 6. The BET surface area of the gel was 580 m² g⁻¹. The desiccant was capable of adsorbing 40% moisture in 80% RH at 30°C. High adsorption capacity of the gel was due to high specific surface area and presence of very low concentration of CoCl₂ in it. Regeneration of the desiccant could be possible by heating at 150°C for a few hours. The results of this study are useful for the preparation of low cost and highly efficient silica desiccant with improved safety from the point of very low cobalt content.

Acknowledgement

The authors are thankful to the Ministry of Environment and Forests, Government of India, New Delhi, for providing research grant vide sanction no. 19/50/2004 RE.

References

- Ahmed A E and Adam F 2007 *Micropor. Mesopor. Mat.* **103** 284
- Balkose D, Ulutan S, Ozkan F C, Celebi S and Ulku S 1998 *Appl. Surf. Sci.* **134** 39
- Brinker C J and Scherer G W 1990 *Sol-gel science—the physics and chemistry of sol-gel processing* (New York: Academic Press Inc) pp 839–880
- Conradt R, Pimkhaokham P and Leela-Adisorn U 1992 *J. Non-Cryst. Solids* **145** 75
- Cossarutto L, Zimny T and Kaczmarczyk J 2001 *Carbon* **39** 2339
- Cunha J C C and Canepa E M 1986; Research Project Report, Fundatec, Porto Alegre, R S, Goncalves M R F and Bergmann C P 2007 *Constr. Build. Mater.* **21** 2059
- Holleman-Wiberg 2001 *Inorganic chemistry* (San Diego: Academic Press) 1st edn, pp. 1475–1479
- Iler R K 1979 *Silica gels and powders—the chemistry of silica* (New York: John Wiley and Sons) p. 462
- Kalapathy U, Proctor A and Shultz J 2000 *Bioresource Technol.* **73** 257
- Kamath S R and Proctor A 1998 *Cereal Chem.* **75** 484
- Krishnarao R V and Godkhindi M M 1992 *Ceram. Int.* **18** 243
- Lender P W and Ruiter R 1990 *Novel inorganic materials and heterogeneous catalysis*. In *Inorganic and metal-containing polymeric materials* (eds) J E Sheats *et al* (New York: Plenum Press) pp. 187–195
- Li X, Li Z, Xia Q and Xi H 2007 *Appl. Therm. Eng.* **27** 869
- Liou T -H 2004 *Mater. Sci. Eng.* **A364** 313
- Luan T C and Chou T C 1990 *Ind. Eng. Chem. Res.* **29** 1922
- Real C, Alcalá M D and Criado J M 1996 *J. Am. Ceram. Soc.* **79** 2012
- Richardson H W 1993 *Cobalt compounds*, in *Encyclopedia of chemical technology* (eds) J I Kroschwitz and M Howe-Grant (New York: John Wiley & Sons) **Vol 6**, p. 778
- Yalcin N and Sevinc V 2001 *Ceram. Int.* **27** 219
- Zhong L and Yang R T 1999 *AIChE J.* **145** 196