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Synthesis of quality silica gel; Optimization of parameters

Hafiz Asghar Ali, Arshad Chughtai and Abdul Sattar.
Engineering Research Division, Institute of Chemical Engineering and Technology, University of the Punjab Lahore.

ABSTRACT

Silica gels were prepared by acidifying the aqueous solution of sodium silicate. In the investigations, effects of pH, mixing rate, temperature of the reactants and specific gravities of the starting materials were studied. One sample was prepared at temperature of 50 ºC. Self indicating silica gels were also prepared.

The silica gels produced were characterized using the standard analytical procedures. Surface area, bulk density, moisture absorptive capacity, water soluble matter, water soluble sulphate, and heat resistance of the prepared samples were determined.

Optimum parameters for the preparation of good quality silica gel were found to be sp. gr. of sodium silicate 1.20 and of sulphuric acid 1.10, finishing pH of the hydro sol at 3, mixing time 18-20 min and reaction temperature of 20 ^{0}C (room temperature).The quality silica gel produced had bulk density 0.46951 g/cm^3, moisture absorptive capacity 32.7% and iodine no. 23.61 and these values were comparable with a good quality commercially available silica gel.

Key words: Sodium silicate, Hydro sol, Hydro gel and Silica gel.

Corresponding address: E-mail, hasghara@yahoo.com
Ph. # +920429231558, +9203349826158

INTRODUCTION

Silica gel is an adsorbent prepared from the coagulation of colloidal solution of silicic acid. The term silica denotes the compound silicon dioxide and encompasses its various forms including crystalline silicas, vitreous silicas and amorphous silicas. The term “Gel” merely indicates the condition of the material at one stage of its manufacture. It is highly porous structure, characterized by uniformity of the arrangement of the pores and their sizes. The pore area of silica gel varies with the method of manufacture.

Silica gel is widely used as a desiccant. Its role as a catalyst support, as a flatting agent in coatings and as a selective adsorbent in column chromatography is well established. It has the application in modification of viscosities and thixotropy of the liquids. Silica gel may also be used for the waste water treatment, atmospheric moisture control, purification of gases and for petroleum refining. [1]

There are several methods to synthesize silica gels. Most commonly silica gels are manufactured by acidifying an aqueous solution of sodium silicate. The material that 1st form is called a hydrosol, the particles of which agglomerate and results in the growth of silica polymers. The hydrosol is typically formed at low pH and if the subsequent washing steps are also conducted at relatively low pH, the final product then has high surface area (> 700 m²/g).When hydrosol ceases to flow like a liquid (the gel time), it is termed as hydro gel.

Interaction of acid with sodium silicate solution produces orthosilicic acid which is an intermediate product of the hydrolysis. It is very unstable substance which readily condenses with itself to give a colloidal polymer of silica sol.

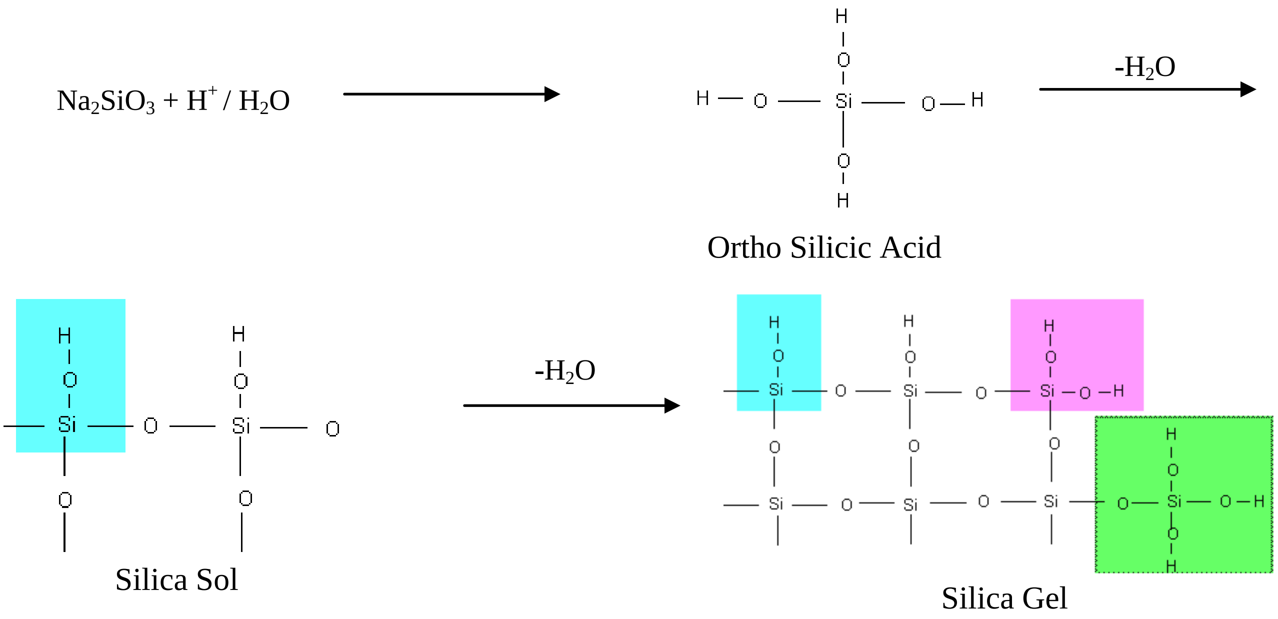

Fig.1 [Different forms of hydroxyl group that can occur on the surface of Silica Gel.]

Further condensation of silica sol takes place on standing which assumes the form of a gel. Silica gel is a continuous three dimensional network of spherical particles of colloidal silica. Both siloxane (-Si-o-Si-) and silanol (-Si-OH) bonds are present in the gel structure. The pores of the gels are interconnected and filled with water from hydrolysis and condensation reaction. [2]

The silanol groups in turn may condense to form siloxane bridges (-Si-O-Si-). Therefore, the surface composition of silica gel (Fig. 2) is made up of physically adsorbed water, chemically bound water and silicon dioxide. [3]

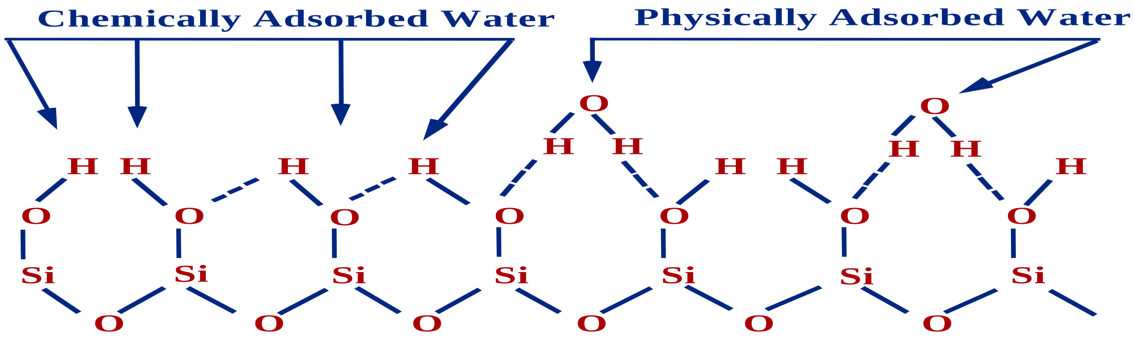

Fig.2 [Silica gel surface showing physically and chemically adsorbed water]

The rate of gelation of silica sol is greatly influenced by the amount of water present, the pH of the sol and the temperature of the contents. The characteristic of silica gel is to shrink on standing during which process known as syneresis, a liquid phase (water) is squeezed out of the gelly. Further removal of water by evaporation produces different grades of silica gel depending upon the number of hydroxyl groups left or removed after dehydration. A typical good quality adsorbent silica gel has a residual water contents of about 6 %, is hydrophilic and has a surface area of 200-800 m^2/gm. [2]

Various methods and raw materials have been employed by a number of researchers [4, 5, 6, 7, and 8] for the preparation of silica gel. Methods for the preparation of spherical silica gel have also been extensively studied [9, 10, 11, 12, and 13].

Silica gels may be examined/analyzed for various applications by determination of their adsorption isotherms. Bulking value, decolourization, dry gas capacity, equilibrium capacity, gas adsorbent tests, hardness, heat of adsorption, heat of wetting, iodine adsorption, retentivity value, water contents, water soluble matter, moisture absorptive capacity and heat resistance are some of the tests carried out on silica gels.[1]

Most of the research work carried out for the preparation of different grades and forms of silica gel exist in patent form and no detailed experimental procedures are available. Therefore it was decided to investigate the parameters responsible for the production of non indicating (white) and self indicating crystalline types of silica gel. The present studies are directed towards establishing the optimum conditions with a view to produce silica gel on pilot plant scale.

2: Experimental

2.1 Materials

1: Commercially available liquid Sodium silicate (sp. gr. 1.43).

2: Concentrated Sulphuric Acid (sp. gr. 1.85).

3: Cobalt Acetate (Merk).

2.2 Preparation of solutions

Concentrated sulphuric acid and sodium silicate were diluted with distilled water to get the required specific gravities. The solutions of sodium silicate and sulphuric acid of specific gravities 1.20 &1.10 were prepared with the help of **"Hydrometer".**

2.3 Procedure

Silica gels were prepared by sol-gel method. Sulphuric Acid (100 gm) of known specific gravity was taken into a beaker with a stirring arrangement. Sodium silicate of known specific gravity was added slowly into the beaker containing sulphuric acid with constant stirring. During addition, the pH level of the hydro sol was noted down after small intervals. When the pH level of the reactants reached at the predetermined mark, the addition of sodium silicate was stopped. The addition of sodium silicate solution into sulphuric acid was completed between time intervals of 18 to 20 minutes. A clear and transparent hydrosol was obtained which was poured into a stainless steel tray. Hydrosol was slowly converted into hydro gel after about few minutes at room temperature. Gel was cut into pieces of about 2 cm with knife. Then the fresh water was added over the hydro gel in the tray and left it for overnight stay.

The next very important step is washing which was carried out before oven drying.

2.4 Washing of silica gel

The sodium sulphate formed during the reaction was removed by replacing the water containing the hydro gel again and again with the fresh water. In order to ensure the complete removal of Na_2SO_4, replacement with fresh water was continued till no turbidity in the shape of $BaSO_4$ appeared on the addition of $BaCl_2$ solution to the washings. The process of removal of salts (sodium sulphate) from the hydro gel took 36-48 hours.

The washing of the hydro gel was necessary in order to get good quality product and optimum yield. If the washing was not done, the product becomes powder on drying.

2.5 Drying

Drying was carried out in order to remove the adhered water from the gel. After washing, the prepared samples of silica gels were placed in an oven at 110ºC for 6-7 hrs. The heating time could be prolonged till constant weight was obtained. On drying, the product automatically disintegrated into transparent crystals of various sizes depending on the experimental conditions.

2.6 Screening

Finally the product was screened in order to get a uniform product. Silica gel of mesh sizes 0.004-5.2mm (3.5-140mesh) was preserved for conducting the different tests. These steps (2.2 to 2.6) were followed through all the experiments conducted for the preparation of samples of silica gel under various conditions. The details of sodium silicate solution used up for 100 gm H_2SO_4 (specific gravities 1.20 &1.10), its specific gravity , pH at hydrosol stage and the weight of silica gel obtained in each experiment has been recorded in Table no. 1.

2.7 Self indicating silica gel

One gram Cobalt Acetate was dissolved in the H_2SO_4 (100 gm) of specific gravity 1.20. This solution was taken into a beaker with a stirring arrangement. Then the solution of sodium silicate (700 gm of sp. gr.1.10) was added slowly into the beaker with constant stirring till the colour of the hydrosol became blue. The washing, drying and screening steps were done by the same procedure as described earlier. After drying the self indicating silica gel, it turned blue in colour. Other colorants were also used to colour the silica gel. e.g. $FeCl_3$ was also used which gave yellow colour in hydrated form while dark brown colour after drying.

3 Characterizations

All the samples of silica gel prepared were characterized for their physical properties (free moisture contents, water soluble matter, bulk density and iodine number) by using standard procedures [1] and the

Values were calculated with the help of equations 1 to 4.

$$\%\ \text{moisture} = \frac{\text{Loss in weight of sample}}{\text{weight of sample}} \times 100 \qquad \text{Eq. (1)}$$

$$\%\ \text{age of water soluble matter} = \frac{\text{Dry weight - Weight after extraction}}{\text{Dry weight}} \times 100 \qquad \text{Eq. (2)}$$

$$\text{Bulk Density} = \frac{\text{Weight of Sample}}{\text{Final volume of sample}}\ \text{g/cm}^3 \qquad \text{Eq. (3)}$$

$$\text{Iodine Number} = \text{m1. titrating 25ml original Iodine solution – ml x Normality of thiosulfate} \qquad \text{Eq. (4)}$$

The iodine number was expressed as the milli equivalent of iodine adsorbed per 100 g of silica gel.
For the determination of heat resistance of silica gel [14], again the iodine no. was calculated by using equation 6.

Water soluble sulphates/chlorides were calculated [15, 16] by using the equation 5.

$$\%\ \text{age of water soluble sulphates / chlorides} = (B/A) \times 100 \qquad \text{Eq. (5)}$$

Where A is the weight of sample taken and B is the weight of precipitates of sulphates or chlorides.
The moisture absorptive capacity of the samples was determined [17] by using the equation 6.

$$\text{Moisture absorptive capacity} = \frac{\text{Increase in weight due to moist air absorbed}}{\text{Weight of sample}} \times 100 \qquad \text{Eq. (6)}$$

The results of all the tests have been reported in the Table no. 2 & Table no. 3. Each experiment was repeated three times and average values have been reported in the tables. The various steps involved for the production of silica gel from sodium silicate and sulphuric acid has been described in the flow sheet diagram Fig. 3.

4 RESULTS & DISCUSSIONS

In the present studies non indicating (white) and self indicating crystalline silica gels were prepared from solution of sodium silicate and sulphuric acid. Silica gels were prepared with different concentrations of the starting materials and at different pH level of the hydrosol. The physical properties of the manufactured silica gel are influenced by the temperature of the reaction, pH level of the hydrosol, concentration and the rate of mixing of the reactants. The properties of the prepared silica gel samples determined included free moisture contents, water soluble matter, water soluble sulphates, moisture absorptive capacity, bulk density, iodine number and heat resistance (Table 2). These were found out with the help of standard test methods [1, 14, 15, 16, and 17] and were calculated by using the equations 1 to 6. Among these, the moisture absorptive capacity and iodine number indicates the extent of surface area existing in the silica gel sample and hence are important parameters for assessing the usefulness of the sample for its industrial applications as a desiccant and catalyst support.

Table no. 1

The effect of finishing pH level of the hydrosol on the weight of silica gel obtained, taking 100 gm of H_2SO_4 of specific gravity of 1.20 and 1.10 at room temperature (20 ^{0}C)

Sample No.	Sp.gr. of Na_2SiO_3	Sp.gr. of H_2SO_4	Final pH of Hydrosol	Wt. of Na_2SiO_3 solution (gm)	Wt. of Silica gel Obtained (gm)	Physical appearance of Silica Gel
1	1.20	1.10	3	140	27.74	Transparent lumps of crystals
2	1.20	1.10	6	170	35.78	Transparent lumps of crystals
3	1.20	1.10	9	300	45.52	Fine crystalline
4	1.10	1.20	2.5	580	No Gel	
5	1.10	1.20	3.5	630	32.02	Transparent lumps of crystals
6	1.10	1.20	6	710	42.22	Transparent lumps of crystal
7	1.10	1.20	9	900	58.01	Fine crystalline

At 50^0 C

8	1.20	1.10	6	166	27.78	Mixed product (lumps of crystals + fine crystalline)

Parametric study of silica gel.

- **Effect of temperature**

The reaction of sulphuric acid with sodium silicate is exothermic and evolves a great amount of heat during the reaction. The reaction was found to be favourable at low temperature to produce good quality product. In order to observe the effect of temperature on the yield and quality of silica gel, the condition of reaction for the preparation of sample no. 2 were repeated at high temperature (50ºC) instead of room temperature(20 ^{0} C) for the preparation of sample no. 8.When the reaction was carried out at this temperature, it was found that the crystalline silica gels (average crystal size 3.4 mm + fines) obtained were of poor quality which had lower transparency, low moisture absorptive capacity (22.1 %), lower iodine number (20.01) compared to the silica gels obtained in sample no. 2 (average crystal size 4.2 mm) having good transparency , moisture absorptive capacity (22.8 %) , iodine number (21.35). Also in the 1st case (at 50ºC) the weight of silica gel obtained was 27.78 gm where as in the latter case (sample no. 2) the silica gel obtained was 35.78 gm.

- **Effect of pH**

The pH at witch the addition of sodium silicate solution was stopped and the resulting hydrosol was allowed to gel was found to have a profound effect on the characteristics of the prepared silica gel. The quality of silica gel was greatly affected by changes in the pH level of the hydrosol. In the preparation of sample 3 and 7 (Table no. 1) where the addition of Na_2SiO_3 into H_2SO_4 (hydrosol) was taken at the high pH level, the fine crystalline products of silica gel were obtained. This may be due the reason that above pH 7 stabilized sol particles grew to radii of about 100 nm which resulted in the separation from each other and fine crystalline silica products were derived. It can also be seen that as the pH level of the hydrosol was left high (samples 3 & 7) ,the weight of silica gel obtained (Fig. 4) was increased where as the % moisture absorptive capacities (Fig. 5) and iodine numbers (Fig. 6)of the prepared silica gel decreased compared to the other samples.

On the other hand, at low pH, aggregation of the particles occurred with the growth of chain length and finally three dimensional gel networks were created. This provided the crystalline silica gel of larger crystal sizes, the sample number 1,2,5,6 & 8 have average particle size of 5.2 mm, 4.2 mm, 4.8 mm, 3.9 mm and 3.4 mm respectively. Sample no. 1 and 5 prepared at pH 3 to 3.5 showed comparable moisture absorptive capacities (32.7 % & 31.9 % respectively) to the commercially available granular good quality silica gel having moisture absorptive capacity 33.0 % (Table no. 3).

While too low pH level of the hydrosol (pH 2.5) resisted the gel formation (Table no. 2). This hydrosol was not converted into hydro gel even after 24 hrs. The control of pH was found to be a major factor for the formation of granular and fine crystalline silica gel.

- **Effect of concentration**

It can be seen from Table 1 & 2 that as the concentration of the solution of Na_2SiO_3 were changed, the characteristics of the final product were also changed. Among the samples of silica gel prepared at pH 3 to 3.5 of the hydro sol, sample no. 1 produced with a relatively concentrated solution of sodium silicate (sp. gr. 1.20) showed better characteristics of moisture absorptive capacity (32.7 %), bulk density (0.46951 gm/cm^3) and iodine number (23.61) compared to the sample no. 5 prepared from a less concentrated sodium silicate solution (sp. gr. 1.10) having moisture absorptive capacity (31.9 %), bulk density (0.45706 gm/cm^3) and iodine no. (23.30).The reverse of this observation can be seen at pH 6 where sample no. 6 prepared with a comparatively weaker sodium silicate solution (sp. gr. 1.10) showed better quality product compared to the sample no. 2 prepared with a more concentrated sodium silicate solution (sp. gr. 1.20).

- **Effect of mixing rate**

Preparation of silica gels was also affected by mixing rate and it was observed that the product quality and crystal size were changed by changing the stirring rate. If the stirring was not done properly, local co-agulation resulted and after drying the hydro gel, amorphous (powder) silica gel was obtained. One experiment was performed by keeping all the parameters constant with respect to experiment no. 1 except mixing time. In this case the reaction was completed in 6-8 minutes which yields small size crystals (average crystal size 1.1 mm) of silica gel. When the addition of sodium silicate solution was slowed down and the reaction was completed in 18-20 min, the hydro gel on drying provided transparent, large size crystals (average crystal size 5.2 mm) of silica gel.

Table no. 2

Physical properties of the prepared silica gel samples

Sample No.	Free moisture contents (%)	Water soluble matter (%)	Water soluble sulphate (%)	Moisture absorptive capacity (%)	Bulk density (g/cm³)	Iodine Number	Heat resistance of silica gels (Iodine No.)
1	2.23	3.67	0.02	32.7	0.46951	23.61	23.45
2	2.90	3.39	0.040	22.8	0.34234	21.35	21.15
3	2.76	9.63	0.036	20.5	0.28912	20.35	20.10
5	2.03	3.97	0.025	31.9	0.45706	23.30	23.05
6	1.55	12.42	0.042	25.4	0.40113	22.10	21.9
7	1.49	15.8	0.034	19.7	0.32499	20.12	20.01
8*	1.40	13.17	0.032	22.1	0.31340	20.01	19.9
9**	2.01	3.11	0.015	33.0	0.48615	23.87	23.80

* Sample No. 8 was prepared at 50 ^{0}C

** Sample No. 9 was the commercially available granular silica gel.

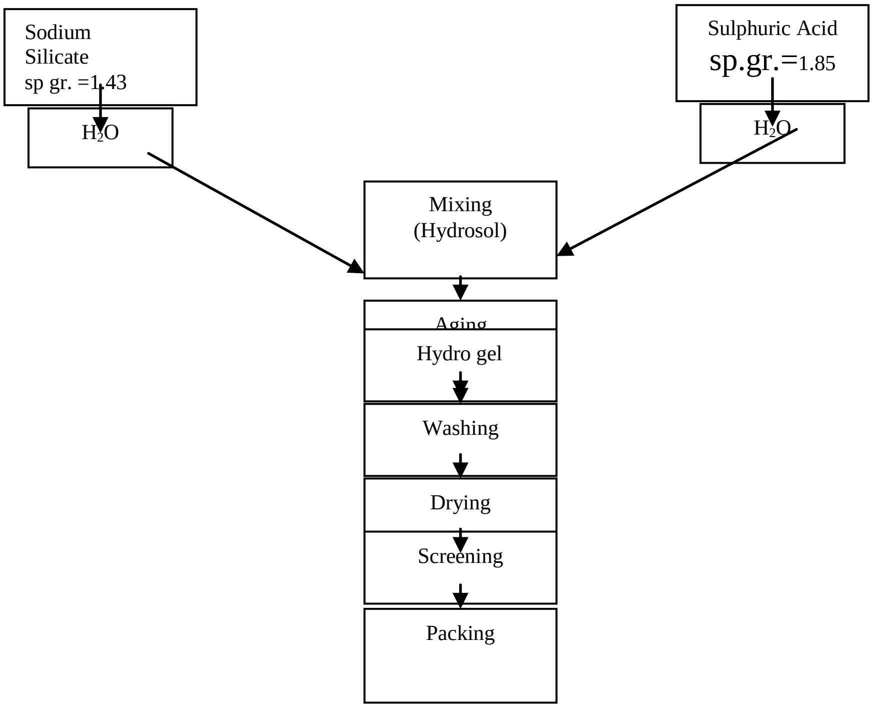

Fig.3 Preparative experimental flow chart for silica gel.

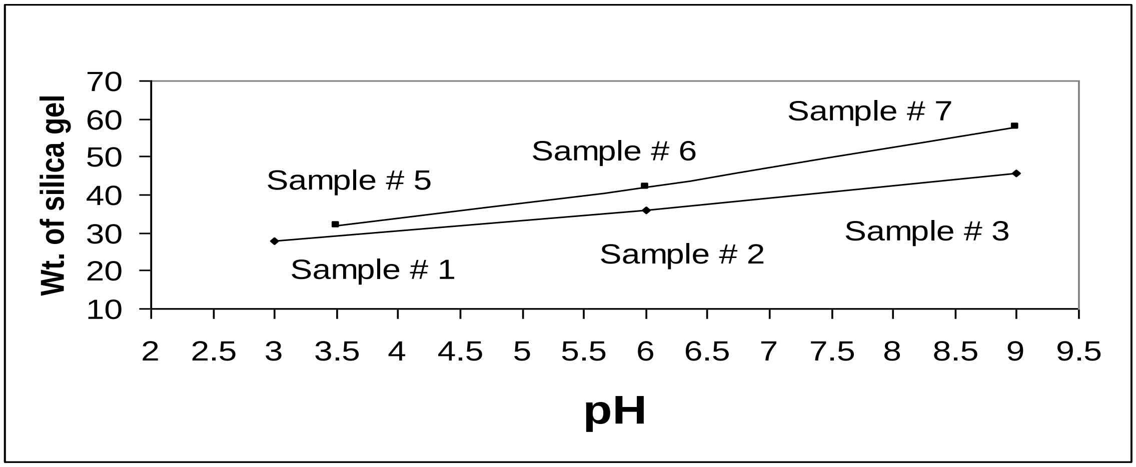

Fig 4. Effect of pH on the weight of silica gel obtained.

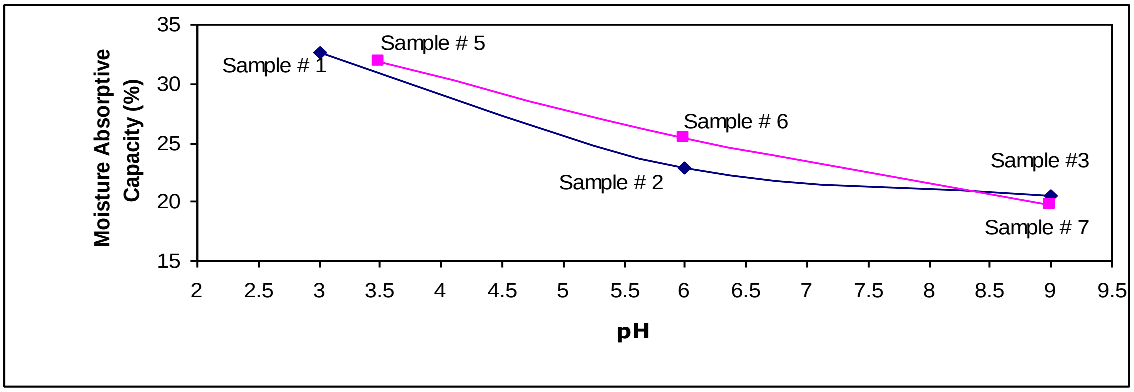

Fig 5. Effect of pH on the moisture absorptive capacity (%) of silica gel

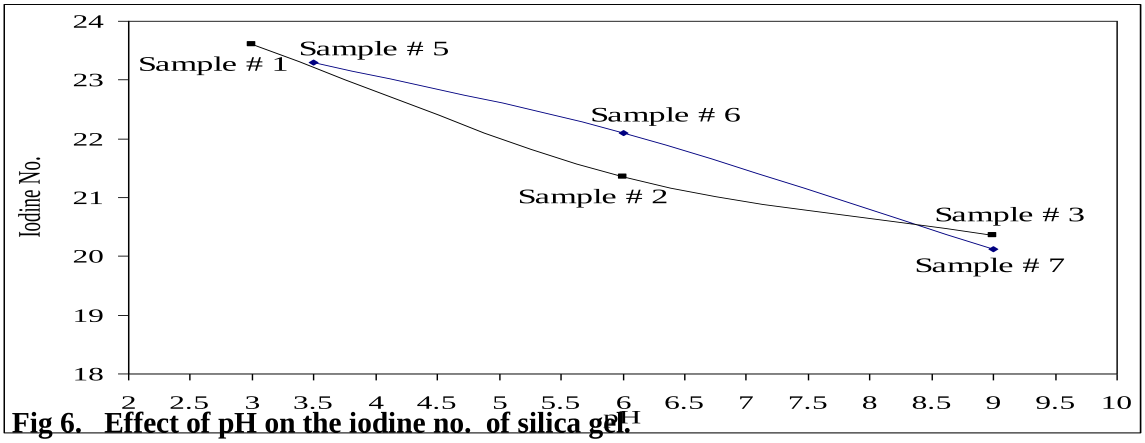

Fig 6. Effect of pH on the iodine no. of silica gel.

The sample no. 1, 2 and 3 were prepared with the solutions of sodium silicate and sulphuric acid of specific gravities 1.20 and 1.10 respectively where as sample no. 5, 6 and 7 were prepared with the solutions of sodium silicate and sulphuric acid of specific gravities 1.10 and 1.20 respectively

The Comparison of free moisture contents, bulk densities, water soluble matter and water soluble sulphates of the prepared samples of silica gel and commercial silica gel (Figs. 7-10).

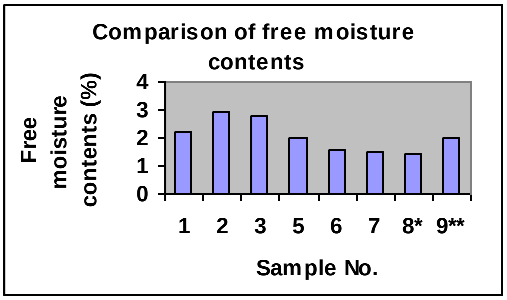

Fig7: Comparison of free moisture contents of different prepared samples of silica gel and commercial silica gel.

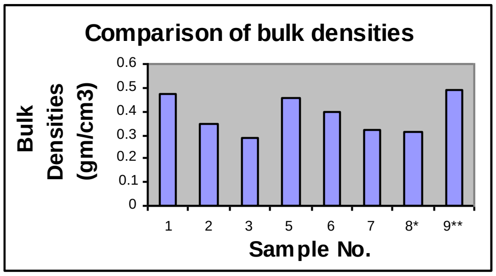

***Fig 8: Comparison of bulk density (g/cm^3) of different prepared samples* of silica gel and commercial silica gel.**

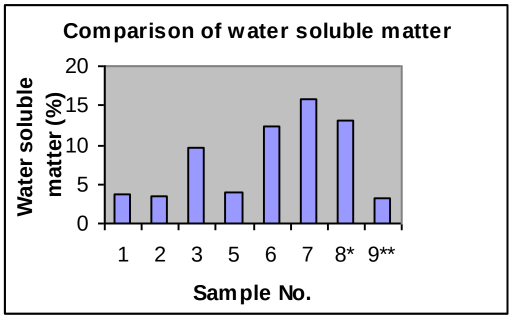

Fig 9: Comparison of water soluble matter of different prepared samples of silica gel and commercial silica gel.

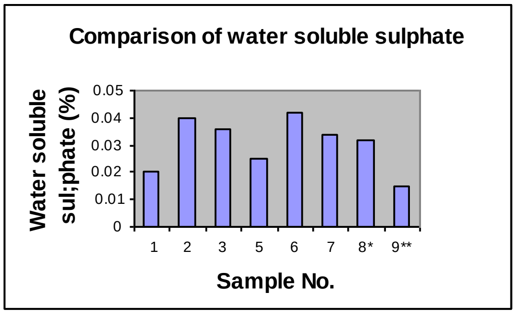

***Fig 10: Comparison of water-soluble sulphates of different prepared samples* of silica gel and commercial silica gel.**

Table no. 3

Moisture absorptive capacity (%) of silica gel

Time (hr)	**Sample # 1 (%)**	**Sample # 2 (%)**	**Sample # 3 (%)**	**Sample # 5 (%)**	**Sample # 6 (%)**	**Sample # 7 (%)**	**Sample #8 (%)**	**Sample # 9 (%)**
1	7..9	14.2	8.8	13.5	14.0	8.6	8.8	8.1
2	12.8	20.2	14.3	20.0	20.0	14.0	12.0	13.2
3	17.3	22.8	20.5	25.8	25.4	19.1	15.1	18.3
4	23.0	22.8	20.5	31.9	25.4	19.7	19.0	24.1
5	28.0	22.8	20.5	31.9	25.4	19.7	22.1	29.4
6	32.7	22.8	20.5	31.9	25.4	19.7	22.1	33.0
7	32.7	22.8	20.5	31.9	25.4	19.7	22.1	33.0

Moisture absorptive capacity was determined using Eq. no. 8.

Graphical representation of moisture absorptive capacity (%) of silica gel.

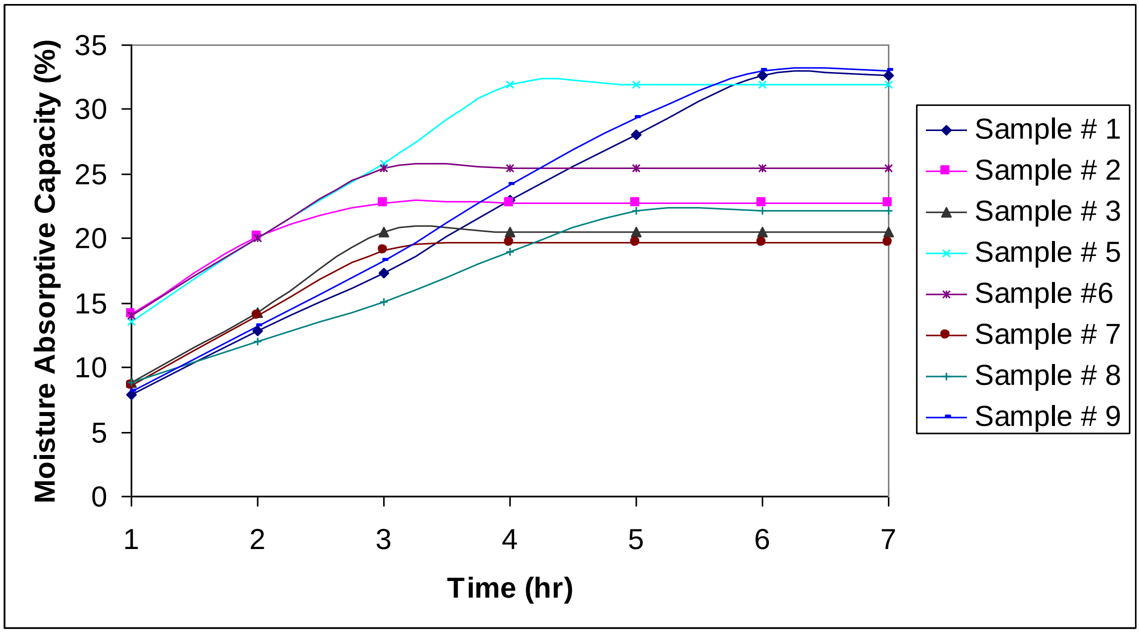

Fig.11:Effect of time on moisture absorptive capacity of different samples.

From Fig. 11 it can be observed that the sample no. 7 has the lowest moisture absorptive capacity (19.7%) and the sample no. 1 has the highest value of moisture absorptive capacity (32.7%) as compared to all other prepared samples.

5 CONCLUSIONS

Non indicating (white) and self indicating crystalline silica gels have been prepared successfully. Sodium silicate and sulphuric acid are used as the starting materials for the manufacture of silica gels. Both starting materials are available in the market at reasonable price as compared to the other raw materials used for silica gel synthesis. These investigations have indicated that there is a great scope for their exploitation as the raw materials for the production of silica gel on industrial scale in the country.

The present study revealed that when the specific gravities of Na_2SiO_3 and H_2SO_4 were kept at 1.20 & 1.10 respectively then the large size crystals of silica gels (average crystal size 5.2 mm) were obtained by keeping the final pH of the hydrosol at 3 and the fine crystalline silica gels were obtained when the final pH level of the hydrosol were kept at 9. It has been observed that the gelling starts in the reaction mixture when the pH level of hydro sol was between 3 and 4. Similarly when the specific gravities of Na_2SiO_3 & H_2SO_4 were kept at 1.10 & 1.20 respectively then the large size crystals of silica gels (4.8 mm) were obtained by keeping the final pH level of the hydro sol at 3.5 and the fine crystalline silica gels were obtained when the final pH level of hydro sol were kept at 9. In this case of study the gelling starts in the reaction mixture when the pH level of hydro sol was between 6 and 7. From Figs. 7 to 10 and Table no. 2, it can be observed that the silica gel of sample no. 1 and 5 have close resemblance to the physical properties of a good quality commercially available silica gel (sample no. 9).The physical properties especially the moisture absorptive capacity, bulk density and iodine number are important parameters for silica gel sample to be useful as industrial adsorbent and a catalyst support.

Sample no. 1 was found to have the best combination of properties among all the samples and the process for the preparation of sample no. 1 can be recommended for the exploitation on pilot plant scale production of good quality silica gel.

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