Effect of Acidic salts on Characteristics of Precipitated Silica from Geothermal Sludge

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Abstract—This research was carried out to produce precipitated silica from sodium silicate using acidic salt as precipitator. The aim of this research is to study the effects of acidic acid on precipitated silica characterization. The sodium silicate solution was produced by extraction of geothermal sludge using sodium hydroxide 2N solution. Precipitated silica products were characterized by x-ray diffraction, x-ray fluorescence and scanning electron microscopy. The results showed that the silica precipitated prepared by aluminum sulfate solution (1-3N) is a silica-alumina composite, amorphous structure and about 0.5 millimicron particle size. Precipitated silica with a concentration of 97.3 w% can be produced from sodium silicate solution using 1-3N sodium dihydrogenphosphate solutions, have an amorphous structure and 1-2 micromicron particle size. Microscopically precipitated silica prepared by aluminum sulfate has a softer structure than that of precipitated silica prepared by sodium dihydrogen phosphate.

Keywords—Acidic salt, precipitated silica, geothermal sludge, silica alumina

I. INTRODUCTION

The production of precipitated silica starts with the reaction of an alkaline silicate solution with a mineral acid. It was also found that ionic strength, over cation identity, determines silica polymerization and particle flocculation rates [1]. From the reaction of silicate solution and mineral acid described previously, different silica products can be formed, namely silica gel or precipitated silica. Patterson [2] have been reported the uses and nomenclature of synthesis silica gels and precipitated silica that are significant commercial importance. The formation of silica gel may be more domination by polymerization from monomers silicic, while precipitated more domination by flocculation and sedimentation of particle silica. Precipitated silica has found various applications as filler in rubber and plastics, absorbent, carrier, drying powder, substrate, catalysts, anticorrosion agent, defoamer, etc. The properties of precipitated silica depend strongly on the conditions of its synthesis, such as the synthesis temperature, time of precipitation, pH, addition of coagulant, and modes of washing and drying. These factors influence the size of the silica particles, their aggregation and specific surface area.

This research was carried out to produce the precipitated silica in addition to knowing the effects of acidic acids on characteristics of silica precipitates. Chen et al [5] reported the preparation of precipitated silica using sulfuric acid as precipitator from sodium silicate prepared by corn straw ash. Sodium silicate solution has also been prepared by geothermal extraction using NaOH solution [2]. The sodium silicate solution commonly is alkaline solution (pH 13-14). Addition of acidic salts with a certain concentration will reduce the pH of the solution. Silicon was exists in the form of SiO$_2^{4-}$ in alkaline solutions and in the form of monosilicic acid if the pH solution value in the range of 1-8 [6]. But if the pH silica solution is below pH 7, the alkaline-silica solution may produce the silica gel. Precipitated silica can be produced at a pH susceptibility above 7. Therefore the concentration and acidic salts volume influence to keep the pH of the alkaline silica solution not below value of pH 7 and produce silica gel.

This study used the acid salt to produce precipitated silica is sodium dihydrogen phosphate (NaH$_2$PO$_4$) and Aluminum Sulfate (Al$_2$(SO$_4$)$_3$). Aluminum salts can react with silica to produce silica-alumina compounds [6]. The morphology of precipitated silica was analyzed by scanning electron microscopy. Meanwhile, to find out the product composition was using X-ray fluorescence and to determine the crystallinity of the product using X-ray diffraction.

II. MATERIALS AND METHODS

A. Materials

Silica source for this study is obtained from geothermal plant, PLTPB Dieng Wonomobo as solid waste, namely geothermal sludge. The XRF analysis on geothermal sludge particles showed that the concentration of silica is 97.3 w% and other components in the form of K$_2$O, CaO, MnO, Fe$_2$O$_3$. Acid salts, aluminum sulfate (Al$_2$(SO$_4$)$_3$) and sodium dihydrogen phosphate (NaHPO$_4$) obtained from chemical distributor CV Medica Vanjaya.

B. Preparation of sodium silicate from geothermal sludge

Geothermal sludge is dried, to reduce water content, and a reduction in size is then sieved with a size of 100 mesh. Sodium silicate prepared by extracting 62 g of geothermal sludge powder with a solution of sodium hydroxide (NaOH) 2 N at 100°C for 60 minutes using hot plate stirrer. The reactions that occur in the formation of sodium silicate are as follows [2]:

$$\text{SiO}_2(s) + 2\text{NaOH}_{(aq)} \rightarrow \text{Na}_2\text{SiO}_3_{(aq)} + \text{H}_2\text{O}(l)$$
250ml sodium silicate solution was obtained from the extraction is then diluted by demineralized water in a ratio of 1: 1; 1: 2; 1: 3; 1: 4 and 1: 5 respectively. From the dilution, the concentration of silica in sodium silicate was obtain in the range of about 2.9; 2.6; 2.1; 1.6; 1.2 w% SiO₂ respectively.

C. Preparation of Precipitated Silica

The sodium silicate is titrated with acid salts according to the concentration in the range of 1-3N until the mixture reaches pH 7. After reaching pH 7 the mixture is allowed to stand until deposition occurs. Then silica separated from filtrate by filtration using wachtman paper. Precipitated silica is dried using an oven at a temperature of 100°C to remove water content in silica precipitate products.

D. Characterization

Silica precipitate products were analyzed using scanning electron microscopy (SEM) to determine the particle morphology, pore diameter, and particle size. X-ray fluorescence analysis for determined the composition of the product and its purity. X-ray diffraction analysis was to find out the classification of crystal structures and product impurities.

III. RESULT AND DISCUSSION

Fig.1. showed diffraction patterns for silica precipitate products before washing prepared by NaH2PO4 (Fig.1a) and prepared by Al2(SO4)3 (Fig.1b). A peak widens was appears from 15 to 25° which indicated the amorphous phase in both product. There appear to be many sharp peaks that indicated the presence of impurities salts in precipitated products, especially precipitated silica product prepared by NaHPO4.

Fig. 2 showed the diffraction pattern of precipitated silica after washing. The washing operation showed that it was able to remove the impurities salts from precipitated silica product. This is indicated by the loss of sharp peaks in precipitated silica product diffraction pattern.

A. Effect of Acid Salt Solution on composition of precipitated silica.

Fig.3. showed the effect of Al2(SO4)3 salt solution concentration on concentration of silica(SiO2) in precipitated silica. Based on the results of XRF analysis (fig.3a), it can be seen that the greater the concentration of sodium silicate from 1.2 to 2.9%, the lower the concentration of silica in the product. The greater the concentration of Al2(SO4)3 solution from 1 to 2 N the silica concentration in product was decreases, but then there is an increase in the concentration of silica product along with the increase in the concentration of Al2(SO4)3 solution from 2N to 3 N. The formation of precipitated silica at the concentration sodium silicate 2.9% and the concentration of 3N saline solution produce a product with a silica concentration of 68.9%. The opposite effect occurs in aluminum concentrations in silica products (Fig. 3b).
The greater the concentration of sodium silicate solution from 1.2 to 2.9%, the higher the concentration of Al₂O in precipitated silica products. On the other hand, the concentration of Al₂O increases with the increase of salt concentration from 1 to 2 N, then the concentration of Al₂O decreases with the increase of Al₂(SO₄)₃ concentration from 2 to 3 N.

The XRF analysis results also showed that in the precipitated silica product prepared by Al₂(SO₄)₃ solution it was proved that the Al₂O element was not lost by the washing operation. There were no sharp peaks in the diffraction pattern as explained previously it can prove that Al₂O binds to silica to form composites while NaH₂PO₄ salts are limited to matrix formation with silica making it easy to wash.

The purity of precipitated silica prepared by NaH₂PO₄ also proves that all phosphate salts can be washed with demineralized water. The highest purity was achieved at low sodium silicate concentrations of 1.2-1.6%. At low sodium silicate concentrations there is almost no effect of salt concentration (1-3N). The greater the acidic salt concentration shows the higher the concentration of silica in the product. A similar phenomenon with the use of Al₂(SO₄)₃ solution for sodium silicate concentration 2.1-2.9%, namely a decrease in silica concentration along with a decrease in salt concentration from 1-2 N but not as sharp as the decrease in the use of Al₂(SO₄)₃. Furthermore, the concentration increases sharply with an increase in salt concentration from 2 to 3 N. Almost all concentrations of sodium silicate from 1.2-2.9% of precipitated silica products can reach 99% purity when using NaH₂PO₄ salt with a concentration of 3N.

Fig. 4. The effect of NaH₂PO₄ concentration on concentration of silica (SiO₂) in precipitated silica product

**Morphology of precipitated silica products**

Fig.5. showed the microscopy of precipitated silica prepared by a) Al₂(SO₄)₃ and b) NaH₂PO₄ using sodium silicate solution concentration of 1.6% at magnification 10000x. Microscopically precipitated silica prepared by Al₂(SO₄)₃ has a softer structure than that of precipitated silica prepared by NaH₂PO₄ 3N solution.
Fig. 6. Morphology of precipitated silica prepared by NaHPO$_4$ using sodium silicate concentration of a) 1.6% and b) 2.6% (Mag. 500x)

Fig. 7. Morphology of precipitated silica prepared by Al$_2$(SO$_4$)$_3$ using sodium silicate concentration of a) 1.6% and b) 2.6% (Mag. 500x)

Fig.7 showed the morphology of the precipitated silica product prepared by NaH$_2$PO$_4$ at magnification of 500. Figures (a) and (b) show the morphology of silica precipitate using a solution of Al$_2$(SO$_4$)$_3$, with a sodium silicate concentration of 1.6% and 2.6%. Fig.7 (c) and (d) show the morphology of silica precipitate using Al$_2$(SO$_4$)$_3$ solution with a sodium silica dilution ratio of 1.6% and 2.6%. The four images show that the greater the dilution ratio of the sodium silicate solution is the denser the particle distance for the two acid salts.

**Distribution of particle size of precipitated silica**

Fig.8. showed the particle size distribution of the silica precipitated silica prepared by Al$_2$(SO$_4$)$_3$ 3N solution with sodium silicate concentration of 2.6% (Fig 8a) and 1.6% (Fig.8b). The determined particle size was with calculation of particle diameter method. Obtained the particle size about 0.5 μm

Fig. 8c showed the particle size of the precipitated silica prepared by NaH$_2$PO$_4$ 3N with a concentration of sodium silicate 2.6% having a size in the range of 1 - 2 μm. Fig.8d showed the particle size of the precipitated silica prepared by NaH$_2$PO$_4$ 3N solution with a sodium silicate 1.6% having a particle size in the range of 1 - 1.8 μm.
IV. CONCLUSION

Precipitated silica concentration of 99% SiO2 can be produced from sodium silicate solution using acidic salts NaH2PO4 solutions, have an amorphous structure and 1-2 μm particle size. Precipitated silica-alumina composite formed by reaction of sodium silicate with Al2(SO4)3 salt solution, amorphous structure and about 0.5 μm in particle size. The silica content in silica precipitated products prepared by NaH2PO4 is higher than precipitated silica particle prepared by Al2(SO4)3 acid salt solution.

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REFERENCES