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Effect of Additives on Preparation of Chlorine Scavenger Powder

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Calcium hydroxide as the principal component was prepared for chlorine scavenger powder by wet process. The influences of different species and amount of silicone oil and surfactants on surface modification of calcium hydroxide were investigated, by using sieve ratio, bulk density, contact angle and SEM. The experimental results indicated that surface modification effect of calcium hydroxide modified by sodium stearate was better than that of sodium dodecyl benzene sulfonate and the suitable dosage was 2 % and that calcium hydroxide powders with the addition of amino silicone oil, emulsifying silicon oil and water-based silicone oil had good modification effect. Considering the operational requirement of powder fire extinguisher, or large bulk density, amino silicone oil and emulsified silicon oil were satisfied the priority selection which the suitable dosage was 3 %. On the basis of above modification, sodium silicate was also used as composite modifier. The results showed that the powders adding 2 % of sodium silicate had ideal dispensability and anti-caking ability that 1 g of calcium hydroxide modified by sodium stearate, emulsified silicon oil and sodium silicate could be absorbed 0.297 g chlorine.

Keywords: Calcium hydroxide, Chlorine, Modification powder, Scavenger.

INTRODUCTION

Chlorine is an important raw material in chemical industry, however, there has been some underlying risks including toxicity, oxide corrosives and combustion-supporting property in the process of manufacture, storage and transportation [1,2]. The fact that chlorine which mixed with inflammable gas or met with open fire, is easily explosive. As the severely hazardous of chlorine leakage [3,4], it is of great importance to find more effective scavenger to eliminate revealed chlorine.

At present, the main ways to deal with the leakage of chlorine involve the following points. **(1) Diversion:** When substantial leakage happened, the liquid chlorine would be diverted to other containers or storage tanks. **(2) Dilution:** The main leakage sources or the storage tanks or containers were squirted water to form water mist, reducing the toxicity. **(3) Soak and hydrolysis:** The small-sized liquid chlorine cylinder, which leaked due to valves were broke during the transport, could be immersed directly into alkaline solution such as calcium hydroxide or water to neutralize. **(4) Decontamination process:** According to the physico-chemical properties of liquid chlorine, chemisorption and physisorption occurred during the decontamination process. Leaked chlorine was transformed into non-toxic or low toxic substances through chemical reaction of chemisorptions, which is interacting with alkaline solution that was formed by alkaline substances such as sodium hydroxide, ammonia and sodium bicarbonate. And then, the alkaline solution was sprayed on the surface of contaminated substrates or pollution region; physical adsorption that recyclable and adsorptive mediums such as adhesive pads and active carbon was utilized to absorb chlorine.

The disadvantages of above mentioned methods including long treatment time, difficult operation, poor contact and incomplete reactions which was embodied in as following [5]: (1) Chlorine leakage accompanied by fires or explosions had caused sprinkling equipments at a standstill. (2) Alkaline solution can't be totally neutralized for the short retention time of injected alkaline solution in the air the chlorine leakage, which the injection quantity outweighed than reaction quantity and which caused secondary pollution. (3) The chemical decontamination car was mainly used to rescue people who have been exposed into the poisonous and harmful circumstance or used to deal with contaminated and specific objects, but leaked gases in the air were usually unable to deal effectively. Therefore, studies on new and high efficient chlorine scavenger are of theoretical and practical significance.

An ideal scavenger in possession of the characters such as high injection velocity, low cost and complete elimination should be conquered the drawbacks of general scavenger [6], accordingly, scavenger powders generally chosen from alkaline and reductive substances, sodium hydroxide, sodium bicarbonate and calcium hydroxide due to the chlorine is acid and oxidative gas. The theoretical calculation indicated that, under the same experimental conditions, calcium hydroxide has relatively good properties compared with sodium hydroxide and sodium bicarbonate, which make calcium hydroxide an ideal scavenger of chlorine.

In general, the preparation of scavenger of chlorine adopted aqueous solution which has shortcoming of high consumption and strong flowability in the practical application. The investigation of powdered solid as a chlorine scavenger became a new trend. Normally, scavenger powder, through high pressure nitrogen, was scattered onto the leakage region, which interacted with chlorine leaking in the air. In order to fulfill operational requirements, the powdered solid whose the reaction ratio and flowability are needed to be further improved.

Until now, a few of countries such as Japan had researched on the chlorine scavenger, but the preparation of key technologies was not published. Luo *et al.* [7] proposed a method that the dissolving of bulk calcium oxide into alkaline solution was concurrently added a certain amount of moisture-proof agents and ketone, eventually obtained 10 μ of calcium hydroxide particle. On the basis of these studies, researchers further studied on preparation of modified calcium hydroxide powder [5]. Bulk calcium oxide as the main component, water, hydrophobic agent and surfactant were added into the reactor under certain temperature range and stirring rate. After filtering, drying, crushing and screening, the obtaining of white modified calcium hydroxide powder, which had many ideal properties such as high reactivity, good fluidity, small particles, large specific surface area, high crystallinity, complete crystal shape, high hydrophobicity and good air permeability. Although the percentage of scavenger reacting with chlorine was more than 80 %, scavenger's humidity resistance and anti-caking needed to be further improved, which incomplete slaking and crystallization of bulk calcium oxide might have significant effected on the properties of modified calcium hydroxide powder. Xia *et al.* [8] improved the preparation of chlorine scavenger whose components included water, calcium hydroxide, sodium dodecyl sulfate, hydroxy silicone oil, contained-H silicone, acetone and sodium silicate. The modified calcium hydroxide powders, average diameter less than 5 μ, prepared by this method had the advantages of high elimination efficiency, waterproofing, moisture-proof, anti-caking, loose texture and good air permeability. Remarkably, It is a somewhat complicated in the operational process and component. Besides, acetone as diluents of coated dryer, it always caused environmental pollution.

On the basis of aforementioned research and the modification studies powder [9,10], it is hoped that calcium hydroxide as the main raw material, with further improvement and research on surface modification, was prepared for an ideal chlorine scavenger.

EXPERIMENTAL

Calcium hydroxide, sodium dodecyl benzene sulfonate (SDBS), sodium stearate (SS1) and sodium silicate (SS2) are all produced by Tianjin Kemiou Chemical Reagent Co., Ltd., emulsifying silicon oil (ESO), water-soluble silicon oil (WSO) and amino silicon oil (ASO) are produced by Jinan Xinyijia Chemical Co., Ltd.

Preparation process: The surfactants and others additives, keeping constant temperature 330 K, were completely dissolved into water in definite proportion to form uniform solution. And then, laminated desiccant and calcium hydroxide were added into the reactor, uniformly stirring the mixture for 0.5 h, filtering, drying, crushing and screening the powders by 400 mesh sieve to obtain modified powders. The variety and dosage of additives in the process of the experiment showed in the following Table-1.

TABLE-1
POWDER CALCIUM HYDROXIDE FOR MODIFICATION OF ADDITIVES AND THE DOSAGE OF ADDITIVES

Type of additives	Name of additives	Dosage of additives (%)
Surfactant	Sodium dodecyl benzene sulfonate (SDBS)	0.5-3.0
	Sodium stearate (SS1)	0.5-3.0
Dispersant	Sodium silicate (SS2)	0.5-3.0
Coated desiccant	Emulsifying silicon oil (ESO)	0.5-3.0
	Water-soluble silicon oil (WSO)	0.5-3.0
	Amino silicon oil (ASO)	0.5-3.0

The amount of additive is relative to the mass fraction of calcium hydroxide.

Characterization of calcium hydroxide powder

Screening mass ratio: Sieving ratio as one of indicators, the mass ratio of screened parts and total weight of objects, was used to reflected effect of modification. The less agglomeration powders were, the more effectively it is.

Bulk density: Bulk density, the mass per unit volume of a substance under specified conditions of pressure and temperature, indicated the degree of surface modification that the higher bulk density corresponded to less agglomeration. Bulk density of the samples was determined through FL4-1 from Jinaipu Technology Co., Ltd, Beijing.

Contact angle: Contact angle of modified calcium hydroxide was measured by the sessile drop method with HARKE-SPCA from Harke Test Instrument Factory, Beijing.

SEM analysis: The shape and entire distribution of modified calcium hydroxide powders can be observed by scanning electron microscopy (SEM) with NANOSEM 430 from FEI TM, America. Good modified powders were usually not exactly like its poor counterpart, the most obvious different being that it had uniform particle size distribution.

RESULTS AND DISCUSSION

Influence of SDBS and SS1 to powder modification

Screening mass ratio: As is shown in Fig. 1, the results showed that screening mass ratio increased drastically at first and then leveled off with the increasing amount of SS1, while the addition of SDBS had little impact on the sieving ratio. In addition, it was found that SDBS whose molecular structure contains benzene rings, had helped to enhance the powders of hygroscopicity, which the agglomeration was caused easily in

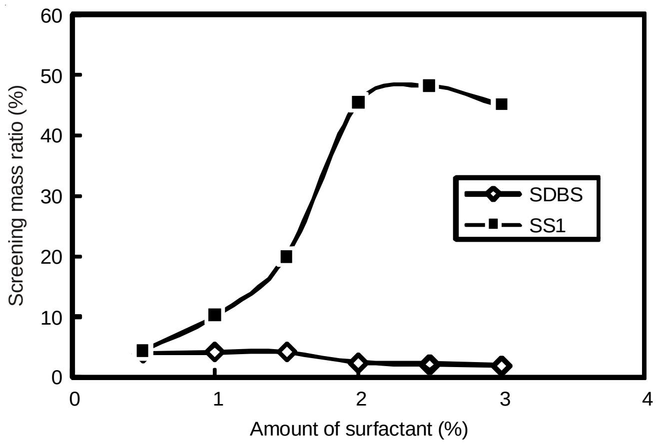


Fig. 1. Screening mass ratio of the samples with different amounts of surfactant

the process of preparation. The experimental results showed were showed that the optimal dosage of SS1 was 2 to 3 %.

Contact angle: It is fact that contact angle directly reflected the hydrophobic property of powder surface. The bigger the contact angle is, the more hydrophobic it is. Fig. 2 showed that contact angle of powders decreased with increasing of addition amount of SDBS. The probable reason of the existence of the phenomenon was the powders surface adhered to the SDBS. The powders modified by SDBS, forming the Pendular liquid bridge among the particles, were easily to absorb moisture in the air on which would enhanced the wetting. The powders modified by sodium stearate whose interfacial tension increased significantly, which were presented hydrophobicity and less agglomeration, had distributed to be stable.

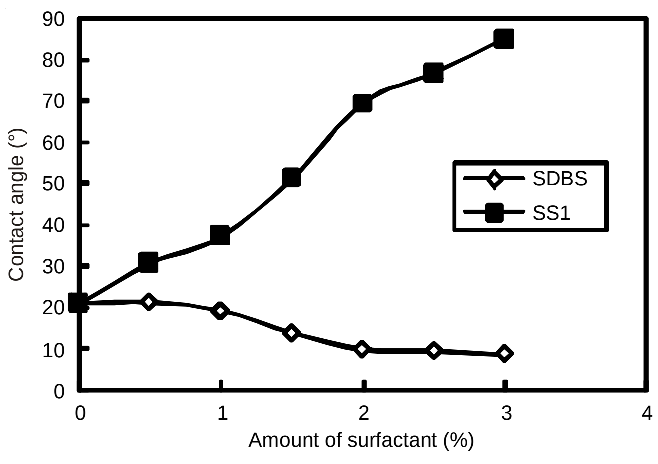
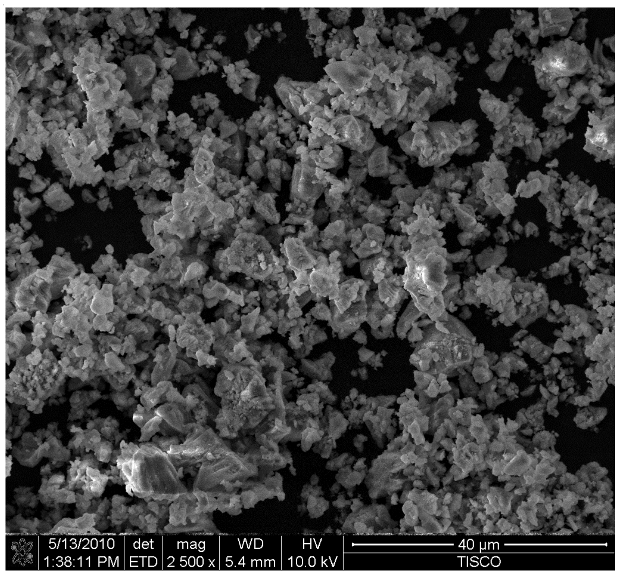


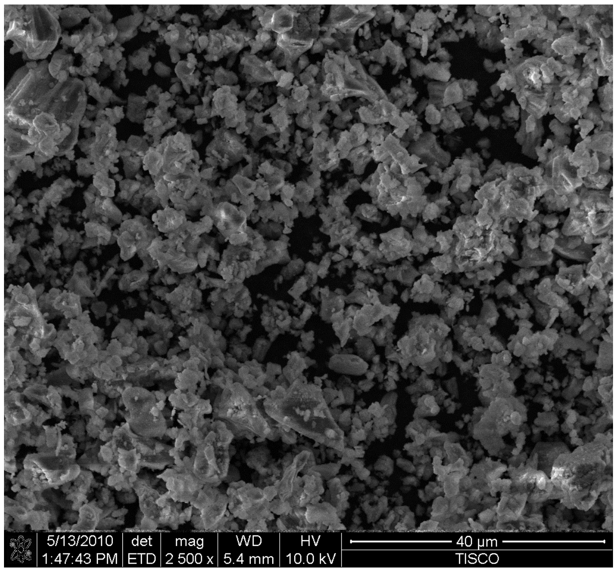
Fig. 2. Contact angles of the samples with different amounts of surfactant

SEM: Fig. 3(a) is SEM photograph of modified powders with 3 % SDBS. Fig. 3(b) is SEM photograph of modified powders with 3 % SS1. From Fig. 3, it can be observed that calcium hydroxide powders modified with SS1 had better dispersion and less aggregation than SDBS.

For above reason, the powders modified with SS1, dissolves easily in water, were usually not exactly like the one with SDBS which would enhanced the wetting processing, macroscopically, it appeared that the presentation of uniform particle distribution and less aggregation would be increased with high screening mass ratio and contact angle.



(a) 3 % SDBS



(b) 3 % SS1

Fig. 3. SEM photos of the samples

Influence of organic silicone oils to powder modification

Screening mass ratio: From Fig. 4, modified powders' screening mass ratio increased with increasing of organic silicone oils, ESO, WSO and ASO, had obvious modification effect on the powders. Moreover, screening mass ratio climbed roughly linearly with the increasing of ESO. In aqueous medium, ESO, uniform dispersion on powders surface, decreased interfacial tension, at the same time, insoluble organosilicon group would be played a role in moisture-proof. Small amounts of WSO, reducing the interfacial tension, which improved stability of powders and enhanced screening mass ratio. Since WSO in possession of larger polar, it can be easily combined with water in the air with increasing of WSO. Amino silicone oil (ASO) whose amino acted with polar groups of powder surface formed hydrogen bonding and organic part worked as water proof, which covered uniformly on powders surface and which effectively inhibited agglomeration and increased screening mass ratio.

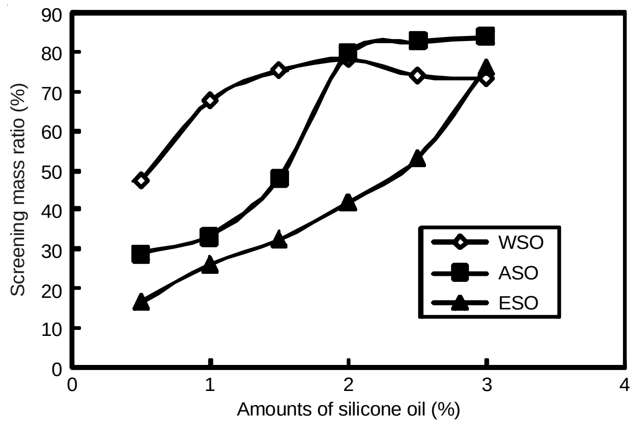


Fig. 4. Screening mass ratio of the samples with different amounts of silicon oil

Contact angle: It can be known from Fig. 5 that the contact angle gradually increased with the amount of the silicone oil when the amount of ASO, ESO and WSO were less than 2 %. However, The contact angle rapidly increased when the amount of ASO, ESO and WSO were greater than 2 %. Contact angle of powder modified by ASO had changed most. It was because ASO had strong hydrophobicity, which led to big contact angle after modification. Surfactant of ESO was hydrophobic, while organic group excluded water, which made contact angle rose slowly. Water-soluble silicone oil (WSO) was hydrophobic and reduced surface tension at the same time, which had little influence on interfacial tension change of powder.

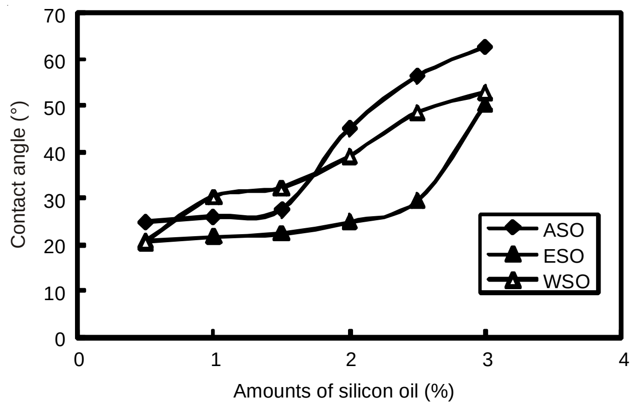


Fig. 5. Contact angles of the samples with different amounts of silicon oil

SEM: In Fig. 6(a) is SEM photograph of powder modified by ESO which was magnified 2500 times. Fig. 6(b) is SEM photograph of powder modified by WSO which was magnified 2500 times. Fig. 6(c) is SEM photograph of powder modified by ASO which was magnified 2500 times. From Fig. 6, it can be known that calcium hydroxide powders modified by three kinds of silicone oils distributed uniformly. However, there was little difference of modification effect among them.

Bulk density: In Fig. 7, WSO had little influence on bulk density that powders trended to fluffy structure whose large space occurring capillary effect easily absorbed water in the air, resulting in the decreasing of bulk density, while the bulk density increased obviously after modifying by ESO and ASO that powders were presented compacted structure.

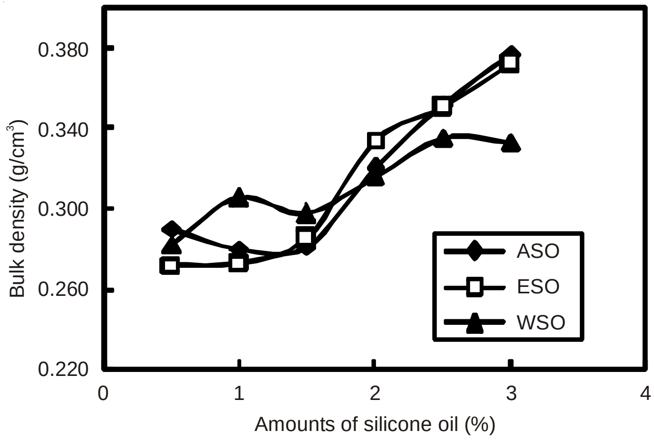
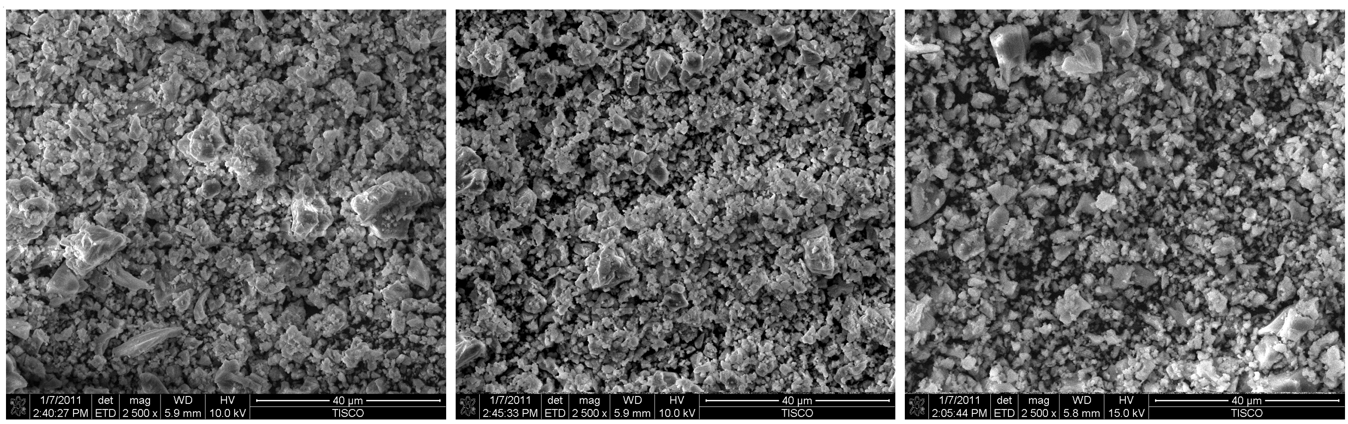


Fig. 7. Bulk density of the samples with different amounts of silicon oil

From the results above, organic silicon oil adding into the powders had good modification effect on screening mass ratio, contact angle and bulk density, Adapted from powder extinguisher requirement on bulk density, the selection of ASO and ESO which the suitable amount was 3 %.

Influence of sodium silicate (SS2) to powder modification: Calcium hydroxide powders adding in the SS2 had better fusion which strengthened modification effect during the wet process. According to the characterization figures, calcium hydroxide powders performed best with 2 % of SS1, 3 % of ASO and ESO. Further research was carried to investigate the influence of adding SS2 on powder modification.



(a) Sample modified with 3 % ESO (b) Sample modified with 3 % WSO (c) Sample modified with 3 % ASO

Fig. 6. SEM photos of the samples

Influence of sodium silicate to screening mass ratio: In Fig. 8, screening mass ratio of composite modified powders improved slightly after adding SS2, which had little influence on screening mass ratio of calcium hydroxide modified powder. Powders modified by SS1, SS2 and ASO whose the screening mass ratio was higher than that modified by SS1 and ESO in the total trend.

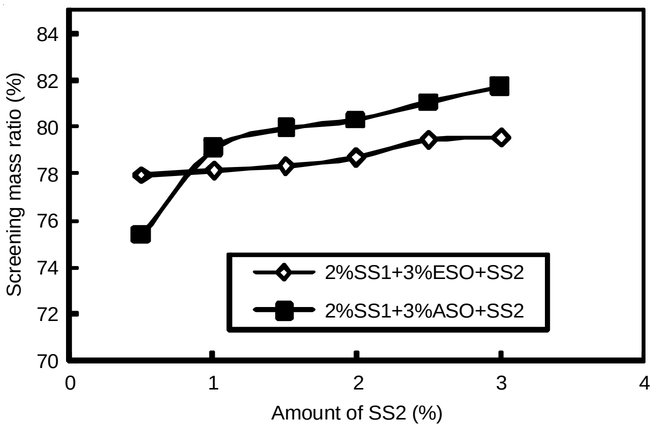


Fig. 8. Influence of sodium silicate to screening mass ratio

Influence of sodium silicate on bulk density: According to Fig. 9, bulk density showed ascending trend after adding the SS2. On the basis of SS2, bulk density of powders modified with ESO was higher than that modified by ASO. When powders modified by SS1 and ESO, the suitable amount of SS2 was 2 %, while powders modified by SS1 and ASO, the suitable amount of SS2 was 2.5 %.

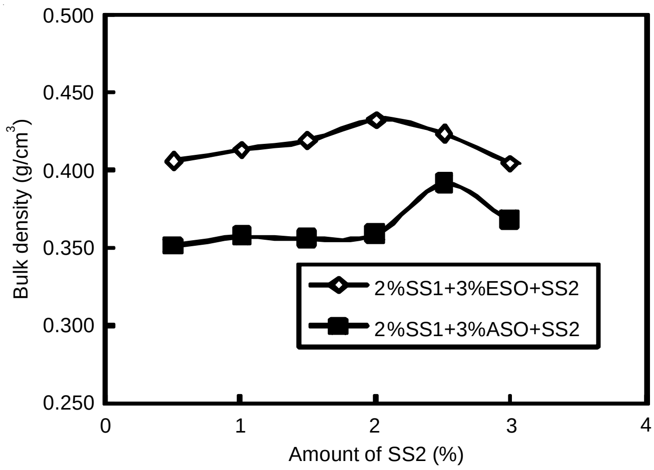


Fig. 9. Influence of sodium silicate on bulk density of calcium hydroxide modified powder

Influence of sodium silicate on contact angle: According to Fig. 10, the contact angle increased with the increasing of SS2. Contact angle of powder modified by ESO was bigger than that of ASO.

SEM of the influence of sodium silicate on powder uniformity: Compared with powder without adding SS2, the shape of powder modified by SS2 was observed by SEM to evaluate SS2 modification effect. The results were shown in Fig. 11.

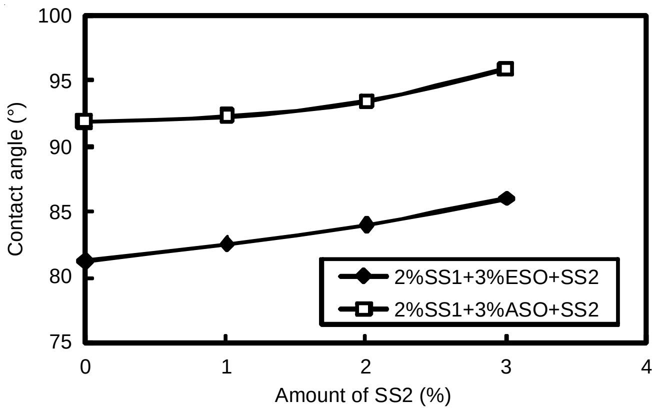


Fig. 10. Contact angles of SS2 solutions on calcium hydroxide modified powder

According to the SEM photos, comparing with calcium hydroxide powder without modification, modified powders were more uniform and less agglomeration. Composite modification had better dispersion and anti-caking ability, after being added 2 % of SS2. So, it can be concluded that sodium silicate had positive effect on composite modified powders which possessed water-proof, anti-caking and loose texture.

Absorption ration of calcium hydroxide modified powder as scavenger to chlorine: Modified powders in the possession of some advantages, water-proof, anti-caking, loose texture and breathable, were investigated in chlorine absorption experiments. The measurement of chlorine absorption ratio was carried out by mass analysis, the chlorine prepared in our laboratory, every 5 min to weight, passed into the modified powder in the tube until the mass of powder would not be increased. And then, the modified powders absorbed chlorine could be calculated by the weight of per gram. The composite modified powders and unmodified powders whose chlorine absorption ration were showed in Table-2.

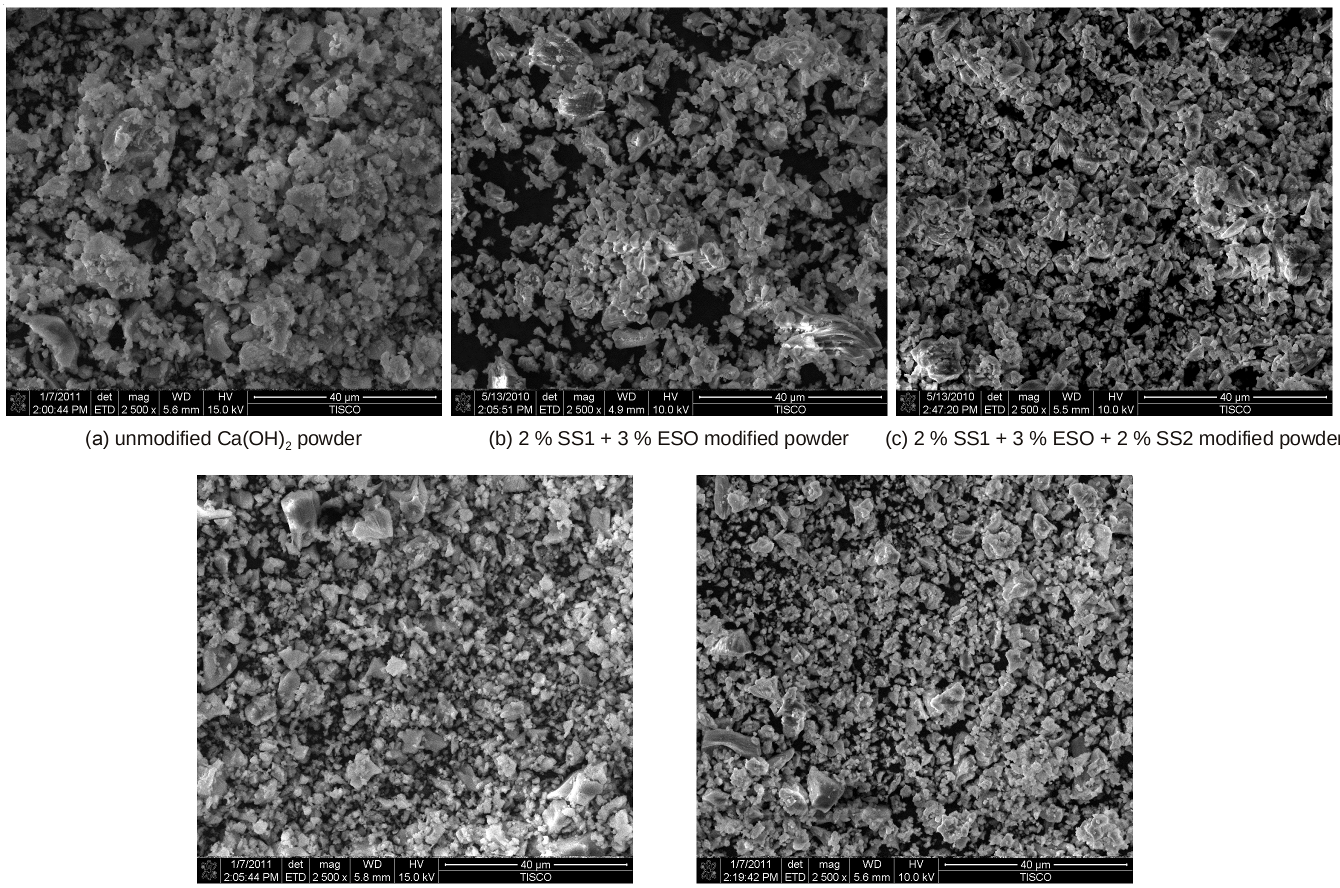
TABLE-2
RESULTS OF CHLORINE ABSORPTION RATIO

Sample	Chlorine absorption ratio (g/g)
$Ca(OH)_2$	0.016
$Ca(OH)_2$ + 2 % SS1 + 3 % ESO + 2 % SS2	0.297
$Ca(OH)_2$ + 2 % SS1 + 3 % ASO + 2 % SS2	0.026

From the Table-2, the composite modified powder' absorption ratio was better than that of unmodified one. The main reason was that the particles of the modified powders trended to uniform distribution and less agglomeration, which improved the efficiency of chlorine absorption. While, the absorption of powder modified by sodium silicate and amino silicone oil didn't obviously increased and the main reason was that organic part of molecules of ASO isolated reaction between calcium hydroxide and chlorine. Therefore, the powders modified with SS1 and ESO both had a good absorption ration and it can be used as chlorine scavenger.

Conclusion

Calcium hydroxide as the main component was modified by several additives to prepare a chlorine scavenger with wet process. The results showed that modification effect of sodium



(a) unmodified $Ca(OH)_2$ powder (b) 2 % SS1 + 3 % ESO modified powder (c) 2 % SS1 + 3 % ESO + 2 % SS2 modified powder

(d) 2 % SS1 + 3 % ASO modified powder (e) 2 % SS1 + 3 % ESO + 2.5 % SS2 modified powder

Fig. 11. SEM photos of the samples

stearate whose optimum adding amount was 2 %, was better than that of SDBS. The ESO, ASO and WSO that the optimum amounts were 3 %, respectively, had good modification effect on screening mass ratio, bulk density and contact angle. On the basis of that, powders in possession of better distribution and anti-caking ability through adding 2 % of sodium silicate. 1 g of calcium hydroxide powder modified by SS1, ESO and SS2 could be absorbed 0.297 g chlorine.

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