

Removal of hydrogen sulfide by zinc oxide nanoparticles in drilling fluid

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ABSTRACT: Hydrogen sulfide is a very dangerous, toxic and corrosive gas. It can diffuse into drilling fluid from formations during drilling of gas and oil wells. Hydrogen sulfide should be removed from this fluid to reduce the environmental pollution, protect the health of drilling workers and prevent corrosion of pipelines and equipments. In this research nano zinc oxide with 14-25 nm particle size and 44-56 m²/g specific surface area was synthesized by spray pyrolysis method. The synthesized nanoparticles were used to remove hydrogen sulfide from water based drilling fluid. The efficiency of these nanoparticles in the removal of hydrogen sulfide from drilling mud were evaluated and compared with that of bulk zinc oxide. The obtained results show that synthesized zinc oxide nanoparticles are completely able to remove hydrogen sulfide from water based drilling mud in just 15 min., whereas bulk zinc oxide is able to remove 2.5% of hydrogen sulfide in as long as 90 min. under the same operating conditions.

Key words: Nano zinc oxide, pollution, hydrogen sulfide, scavenger, absorbent, acid gas

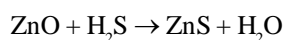
INTRODUCTION

Large quantities of hydrogen sulfide (H₂S) are produced in gas and petroleum industries. It is a corrosive (Duan *et al.*, 2007; Perdomo *et al.*, 2002; Ren *et al.*, 2005) and highly toxic gas and it can be regarded as a major source of air pollution (Haimour *et al.*, 2005). According to the international environmental regulations, H₂S contained in the acid gases should be effectively removed before emission to atmosphere.

H₂S diffused into the drilling fluid, is produced by Sulphate reducing bacteria (SRB) in sea water or in formation water (connate water) under anaerobic conditions where the SRB grow with organic materials such as crude oil as a substrate (Sandnes and Hundvag, 2002). Hydrogen sulfide is a colorless gas and low concentrations of it in air smell like rotten eggs. Its characteristic odor is perceptible in fresh air in a dilution of 0.002 mg /L of air. However the human sense of smell quickly becomes fatigued and may fail to give warning of higher concentration. Coma, collapse and death from respiratory failure may occur within a few seconds after one or two inspiration of the undiluted

gas (Ferguson, 1975). H₂S can be present in drilling mud/water either as H₂S, HS⁻ or S⁻², depending on the pH value (Sandnes and Hundvag, 2002). To protect the health of drilling workers, the concentration of this gas should be reduced to less than 15 ppm (Davidson, 2004).

Various absorbents have been used in industry to remove H₂S from different media (Jung *et al.*, 2006; Li and King, 2006; Ros *et al.*, 2007). Zinc compounds such as zinc oxide (ZnO) and zinc carbonate are common scavengers to remove H₂S from drilling fluids (Davidson, 2004). ZnO is a commodity sorbent and good candidate for the removal of H₂S in drilling fluids, because it has high zinc content (80%) and has well predictable reaction kinetics and absorption capacity. It is also readily available compared with other sorbents, such as molecular sieves or zinc-titanium oxide. H₂S absorption by ZnO is actually controlled by the following reaction that forms inert insoluble zinc sulfide (Bagreev *et al.*, 2001; Sun *et al.*, 2007):



ZnO nanoparticles have large surface area and high

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surface activities. These important key characteristics provide a wide range of potential application in various industries (Hong *et al.*, 2006; Lee *et al.*, 2008; Wang *et al.*, 2008). Spent ZnO sorbent is considered nonhazardous for solid waste disposal (Sun *et al.*, 2007). ZnO nanoparticles are being used in personal care products and the toxicity of these and bulk ZnO has been investigated on fresh water microalga. The chronic toxicity of ZnO nanoparticles has been statistically similar to that of bulk ZnO (Frankline *et al.*, 2007). Given the above findings, it was decided to investigate the performance of nano ZnO as a H₂S scavenger in drilling fluids.

MATERIALS AND METHODS

Bulk zinc oxide with purity of 99.5 % was supplied from Pars company (Iran). Zinc oxide nanoparticles used in this work were synthesized by spray pyrolysis method (Ghaffarian *et al.*, 2008; Okuyama and Lenggoro., 2003) and were characterized by x-ray diffraction (XRD, PW 1840, Phillips, Netherland), scanning electron microscope (SEM,S-360, Cambridge, England), atomic force microscope (AFM, P47H, NT-MDT, Russia) and transmission electron microscope (TEM, AT-210, Bruker, Germany).

Three samples were synthesized with different surface areas and were designated Snano 1, Snano 2

and Snano 3. Fig. 1 illustrates the TEM image of Snano 1. The phase analysis of above samples were performed by XRD and identification of the phases were carried out by using International Center Diffraction Data (JCPDS 36-1451).The diameter of ZnO nanoparticles was calculated using Debye-Sherrer equation.The specific surface area (SSA) of the samples and bulk ZnO were measured by N₂ adsorption method, using BET technique (Quantasorb Model LMFE-7, USA). The physical characterization of ZnO nanoparticles and bulk ZnO used in the experiments are summarized in Table 1. The amount of removed H₂S in drilling mud by nano ZnO was measured according to the following procedure at room temperature.

125 mL water based drilling mud and 125 mL water were poured into a beaker. After adding 1.5 g sodium sulfide nonahydrate (equivalent of about 800 ppm H₂S), the slurry was homogenized by stirring for 30 min. 50 mL of this solution was then taken out, filtered and used as blank. 3.42 g ZnO nanoparticles were added to the rest of slurry and stirring was continued. 50 mL aliquots of the slurry were taken out at intervals of 10 and 15 min. and filtered. The amount of removed sulfide in blank and filtrates were measured using, a standard method (APHA, 1998).

The experiment was carried out for Snano 1, Snano 2, Snano 3 and bulk ZnO respectively. Since the

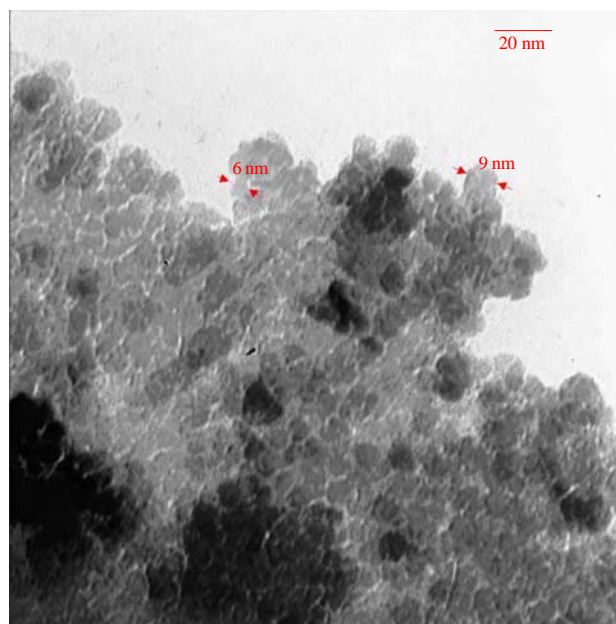


Fig. 1: TEM image of ZnO nanoparticles (Snano 1 sample)

Table 1: Physical characterization of synthesized ZnO nanoparticles and bulk ZnO

Sample	Crystal size (nm)	SSA (BET) (m ² /g)	Phase (XRD)
Snano 1	15	51	Wurtzite
Snano 2	25	44	Wurtzite
Snano 3	14	56	Wurtzite
Bulk ZnO	243	5	Wurtzite

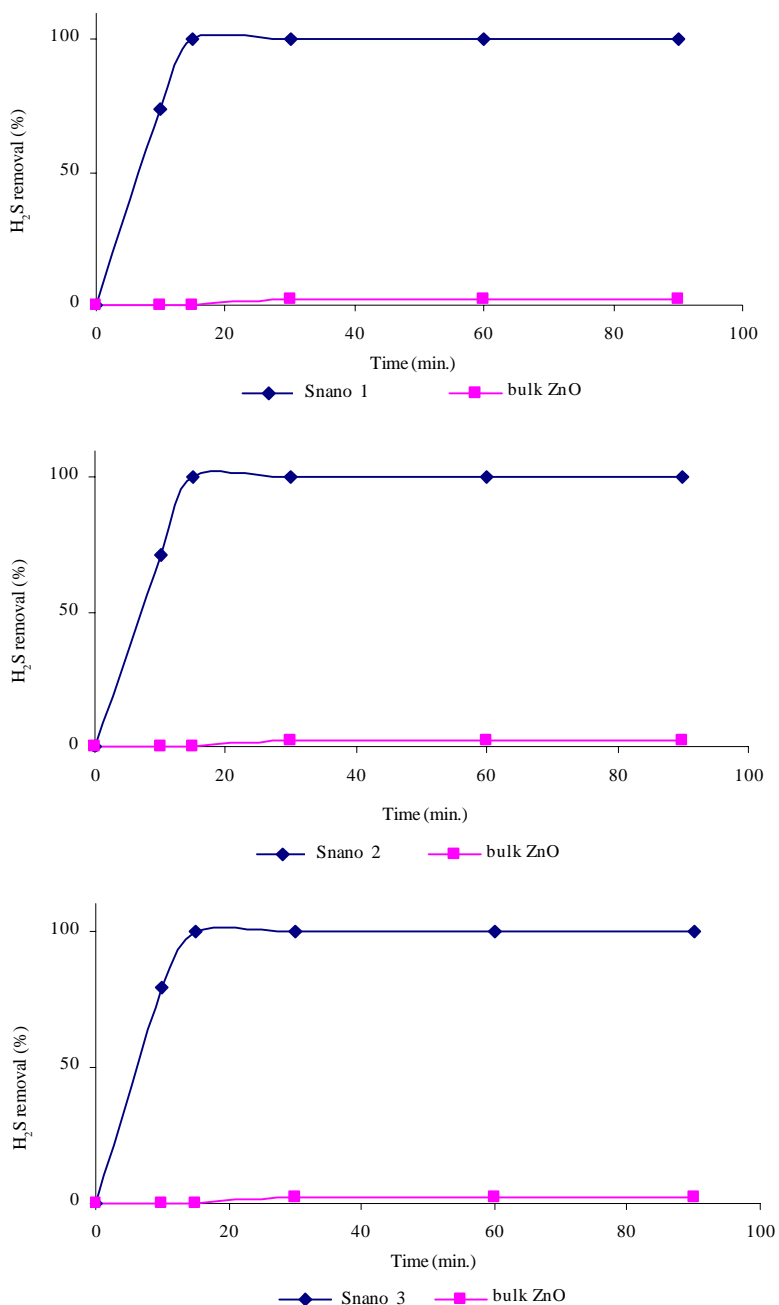


Fig. 2: comparison of H₂S amount removed by ZnO nanoparticles and bulk ZnO

Table 2: The percentage of scavenged H₂S by nano ZnO samples and bulk ZnO

Sample	Blank	10 (min.)	15 (min.)	30 (min.)	60 (min.)	90 (min.)
Snano 1	0	73.5	100	–	–	–
Snano 2	0	71.0	100	–	–	–
Snano 3	0	79.0	100	–	–	–
Bulk ZnO	0	–	–	2.5	2.5	2.5

absorption rate of bulk ZnO was low. The sampling was done in 30, 60 and 90 min. intervals, respectively.

RESULTS AND DISCUSSION

The amounts of scavenged H₂S by ZnO nanoparticles and bulk ZnO in water- base drilling mud is shown in Table 2. Investigation of Tables 1 and 2 indicates that, as the specific surface area of nanoparticles increases from 44 to 56 m²/g, the amount of scavenged hydrogen sulfide increases from 71 to 79 % after 10 min. All nano samples completely remove H₂S from mud after 15 min., whereas bulk ZnO removes 2.5 % of H₂S in as long as 90 min. The ability of ZnO nanoparticles in comparison with bulk ZnO to remove hydrogen sulfide in water- base drilling mud has been shown in Fig. 2.

As shown in Fig. 2, there is a remarkable difference between the rates of H₂S absorption on nanoparticles and bulk ZnO. According to Fig. 1, nanoparticles have a very high porosity, which results in their high surface area and pore volume, therefore; they can scavenge H₂S much faster than bulk ZnO. Since ZnO has also been used as an effective scavenger for removing soluble sulfides from oil-based muds (Garrett *et al.*, 1988), nano ZnO can also be used in such muds. The obtained results in this research show that, ZnO nanoparticles in the range of about 14-25 nm size are reliable scavengers to effectively remove H₂S and soluble sulfides from drilling fluids. Superior performance of nanoparticles in the elimination of H₂S will decrease consumption of bulk ZnO, which will result in minimizing the environmental pollution and lower consumption of natural resources

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