

# Investigating The Effect Of Hydrochloric Acid On Manganese Tetraoxide Water Based Drilling Fluid

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**Abstract**—A research work was carried out to investigate the effect of hydrochloric acid on manganese tetraoxide water-based drilling fluid. Filter cake was produced using the HPHT (High pressure, High temperature) filter press machine and the cake was dissolved in various HCl concentrations ranging between 1-10 wt% at various temperatures. Results obtained indicates that only dissolve of filter cake at 10 wt% HCl was possible at ambient temperatures. At elevated temperatures, above the acid concentration of 3 wt%, there was formation of chlorine gas. It was also noticed that dissolution times decreased with increasing temperature. Therefore, for optimum utilization and environmental safety, HCl concentration should not exceed 3 wt% especially at high temperature.

**Keywords**—Hydrochloric acid, Manganese tetraoxide, Water based drilling fluid, HPHT, Ambient temperatures, Filter cake, Elevated temperatures, Concentrations.

## I. INTRODUCTION

The rotary drilling of a wellbore is accomplished by rotating a drill string having a drill pipe and a drill bit at its lower end. Weight is applied to the drill bit while it is rotating to create a borehole into the earth. The drill string is hollow and sections are added to the drill string to increase its length as the borehole is deepened. This rotary drilling process creates significant amounts of friction which produces heat along with fragments of the strata being penetrated. The fragments of the strata must be removed from the borehole and the drill bit must be cooled to extend its useful life. Both of these functions are accomplished by circulating a fluid down through the drill string and up to the surface between the drill string and the wall of the borehole. Generally, the borehole into which the casing or

liner is introduced is filled with drilling mud. While the use of manganese tetroxide (MnO) in drilling fluid formulations is known, the use of such MnO-containing formulations has generally been found to be damaging to the reservoir formation. Generally speaking, the permeability of reservoirs is reduced when they are contacted with drilling fluids and, as a result, the development of special and expensive stimulation techniques has proven necessary. In horizontal wells, long-reached wells, and in maximum reservoir wells, the stimulation techniques which effectively remove material to restore permeability to the damaged reservoir are not possible since the fluid stimulation acids only contact one side of the reservoir formation due to the effects of gravity. Thus, all of the sides of the wellbore would not be contacted. Drilling fluid or mud is a vital component in the rotary drilling process. It plays an important part in any drilling operations. Some of the main functions of drilling fluids are as follows: to remove drill cuttings, control formation pressures, maintain wellbore stability, cool and lubricate the bit, transmit hydraulic horse power to the bit and to prevent the entry of the subsurface fluids into the annulus. Several advantages and limitations are associated with weighting materials used in drilling fluids such as bentonite, barite, calcium carbonate and manganese tetraoxide. Barite and Bentonite are not soluble in hydrochloric acid (HCl) and as a result of that, they cause formation damage. Additionally, because of the associated heavy metal components including Lead, Cadmium, Arsenic with Barite, it is considered one of the biggest sources of pollution. However, a high density and acid-soluble option is Manganese

tetraoxide ( $Mn_3O_4$ ). To dissolve filter cake, HCl is the most economical and most commonly used cleaning fluid. The reaction of HCl with manganese oxides is quite complex. Some of the reaction products have low solubility in water and can cause formation damage while others are corrosive and evolve strong oxidizers such as chlorine gas. Therefore, extensive laboratory testing is needed before selecting HCl concentration that can be safely and effectively used to remove filter cake formed by manganese tetraoxide-based drilling fluids. Use of high HCl concentrations to dissolve  $Mn_3O_4$ -based filter cake will result in corrosive environment and release of poisonous chlorine gas (i.e., strong oxidizer). Thus, removal of deposits formed at the wellbore because of drilling fluids becomes more challenging when dealing with additives (eg,  $Mn_3O_4$ ) that involve complex interactions with the cleaning fluids, especially at high temperatures. Environmentally friendly dispersants for HP/HT aqueous drilling fluids containing  $Mn_3O_4$ , contaminated with cement, rock salt and clay (Y. Kar et al. 2011). Dispersants are widely used in drilling fluids to prevent solids flocculation and to control the rheological properties of the fluids. There is high demand for effective, thermally stable and environmentally friendly dispersants for HPHT drilling fluids. This work was undertaken to investigate the use of environmentally friendly dispersants in HPHT aqueous drilling fluids containing manganese tetraoxide ( $Mn_3O_4$ ) as the weighting agent. The dispersants were chosen because they are non-toxic to aquatic organisms and biodegradable. The effects of cement, rock salt and clay particles as contaminants on the dispersant performance and the fluid properties were investigated. The dispersants were lab tested in high density fluids of 2.1 g/cm<sup>3</sup> at a temperature of 200°C and pressure of 500 psi. The fluids were analyzed before and after heat-aging using rheometer, sag test, light scattering, and HPHT fluid loss.

This paper evaluated dispersants for high density invert-emulsion drilling fluids weighted with manganese tetraoxide ( $Mn_3O_4$ ) particles for high temperature applications. Additionally, the use of dispersants to control the reaction of cleaning fluid with  $Mn_3O_4$ -based filter cake was studied. The dispersants selected are non-toxic to aquatic organisms and biodegradable. Adding dispersants

to the drilling fluid will result in reduced sag, rheological properties, and low fluid-loss.

$Mn_3O_4$  particles have been used in cementing, drilling, and completion fluids for more than 20 years. Examples of field applications include drilling the reservoir section of the Gullfaks field using potassium formate drilling fluids up to 14 lbm/gal (Howard 1995; Svendsen et al. 1995) and drilling of the North Cormorant field in the North Sea using oil-based drilling fluids (Franks and Marshall 2004; Kleverlaan and Lawless 2004). Moroni et al. (2008) reported laboratory studies and case histories in the UK and Kazakhstan for manganese tetraoxide-based invert-emulsion fluids (11.7 lbm/gal) that showed low filming tendency.

Manganese tetraoxide ( $Mn_3O_4$ ) has been recently used as weighting material for water-based drilling fluids. It has a specific gravity of 4.8 gcm<sup>-3</sup>, making it suitable in muds for drilling deep gas wells, the filter cake formed by this mud also contains  $Mn_3O_4$  (Moajil et al., 2008).

Several articles concerning the use of manganese tetraoxide with other additives in drilling fluid formulations have reported negative effects on the reservoir performance. The permeability of reservoirs is reduced when they are contacted with such drilling fluids, meaning special and expensive stimulation techniques have been proven to be necessary.

Unlike  $CaCO_3$ ,  $Mn_3O_4$  is a strong oxidant (Moajil et al., 2008), hence the use of HCl is not recommended for the removal of the filter cake except at low temperatures. Various organic acids, chelating agents, and enzymes, have been tested at temperatures up to 150°C.

Research has been presented which indicates that a drilling fluid formulation containing manganese tetraoxide causes a minimal reduction of the permeability of the reservoir formation with respect to hydrocarbon flow (Al-Yami, 2009). These formulations are particularly useful for wells that are otherwise difficult to stimulate. A return permeability of 90% or greater was achieved without the need for acidizing treatments.

In order to achieve these performance levels, the formulation must possess certain rheological, density, temperature, and fluid loss properties. Recall that manganese tetraoxide has a density of 4.7gcm<sup>-3</sup>. In comparison to a synthetic mud based on alkalis salts of formic acid, where a return

permeability is 66% of the initial volume of oil injected, in a manganese tetraoxide based mud a return permeability is 93% (Al-Yami, 2009).

### Manganese Oxides Properties and Applications

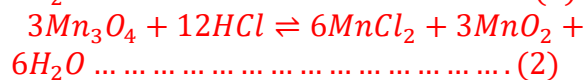
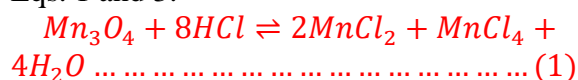
Manganese is an element in the first (3d) transition series and the odd number of electrons in this shell results in an electronic paramagnetism. Divalent manganese has a half filled 3d electron shell, which makes it the most stable manganese and thus, Mn+3 is easily reduced to Mn+2. Manganese has various valences from zero to seven and under normal conditions only the +2, +4, and +7 are important (Schuman 1971; Greenwood and Earnshaw 1997; Vadim et al. 2007).

Six stoichiometric oxides of manganese are known: MnO, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>5</sub>O<sub>8</sub>, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, and Mn<sub>2</sub>O<sub>7</sub>. All hydroxides and oxides of manganese form Mn<sub>3</sub>O<sub>4</sub> when heated to 1,000°C (Kemmitt and Peacock 1973). Mn<sub>3</sub>O<sub>4</sub> forms in nature as the mineral hausmannite (Weiss 1977). Hausmannite [Mn<sub>3</sub>O<sub>4</sub> or (Mn<sup>2+</sup>)(Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>], a distorted spinel oxide mineral with Mn<sup>2+</sup> in tetrahedral coordination and Mn<sup>3+</sup> in distorted octahedral coordination, is a metastable intermediate in the oxidation of soluble Mn(II) to form thermodynamically-stable MnO<sub>2</sub> (Peña et al. 2007). Particle size and temperature affect the oxidation properties of Mn<sub>3</sub>O<sub>4</sub>. Using thermal gravimetric technique (TGA), Gillot studied the effect of particle size of Mn<sub>3</sub>O<sub>4</sub> particles on the oxidation to α-Mn<sub>2</sub>O<sub>3</sub>. He noticed that at low heating rate (3°C/hr) and small particle size, two metastable manganese oxides exist, a cation deficient spinel (Mn<sub>2</sub>O<sub>2</sub>) with Mn<sup>2+</sup> ions oxidation and Mn<sub>5</sub>O<sub>8</sub> associated to Mn<sup>3+</sup> ions oxidation (Gillot et al. 2001). Mn<sub>3</sub>O<sub>4</sub> has been proposed as a cheap, environment-friendly catalyst for the oxidation of CH<sub>4</sub>, corrosion-inhibiting pigment for epoxy polyamide, and in top coating applications (Mu et al. 2006).

### Reactions of Manganese Oxides With Hydrochloric acid

Manganese oxide deposits dissolve in concentrated (~ 12 N) or dilute (~ 3 N) HCl solutions. Dilute solutions should be heated (e.g., 100°C) to be effective in dissolving manganese oxides. The reaction of HCl with manganese oxides are irreversible (Vadim et al. 2007) and depend on the stoichiometry of the reactants. De

(1975) reported Eq. 2 and Vernon (1891) reported Eqs. 1 and 3:



MnCl<sub>4</sub> will decompose and give MnCl<sub>2</sub> and poisons/corrosive chlorine gas. Therefore, as reported by Depourdeaux (1904), Eq3 becomes:



Moreover, in acidic solutions Mn<sub>3</sub>O<sub>4</sub> associate with dissolved chlorine as (Mn<sub>3</sub>O<sub>4</sub>)<sup>2+</sup> ions in (Auger et al. 1991). Chlorine is partially soluble in water and a strong oxidizing agent. Its solubility increases in alkaline solutions. Many interactions in Mn<sub>3</sub>O<sub>4</sub> with cleaning fluids could be due to the tetragonal symmetry of Mn<sub>3</sub>O<sub>4</sub> (Chern et al. 2000). Fe<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> have similar crystalline structure but different curie temperatures, 858 and 43<sup>0</sup>K respectively. Therefore, magnetization of Mn<sub>3</sub>O<sub>4</sub> decreases with temperature (Chern et al. 2000).

## 2. METHODOLOGY

### Materials

All reagents and equipment used in this study are of analytical grade obtained from Chemistry and Petroleum engineering laboratories Abubakar Tafawa Balewa University Bauchi, Bauchi State, Nigeria, unless otherwise indicated. Water-based drilling fluid weighted mainly with Mn<sub>3</sub>O<sub>4</sub> was prepared under static condition (125 RPM) in the laboratory. Starch was added to the mud to control fluid loss and rheological properties of the drilling fluid. The function of lime Ca(OH)<sub>2</sub> and Potassium hydroxide (KOH) is to adjust the PH. Sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) was also added as an oxygen scavenger.

The following reagents and equipment were used for the experiment:

- Diluted HCl solution
- Manganese tetraoxide (Mn<sub>3</sub>O<sub>4</sub>)
- Raw water
- Starch (Cassava Starch)
- Potassium Chloride (KCl)
- Potassium Hydroxide (KOH)

- Calcium Hydroxide (Ca(OH)<sub>2</sub>)
- Calcium Carbonate (CaCO<sub>3</sub> (Fine))
- Sodium Sulphite (Na<sub>2</sub>SO<sub>3</sub>)

**Equipment**

- Retort stands with clamp
- Round bottom flask (250ml)
- Magnetic stirrer
- Glass funnel
- Plastic containers (buckets and bowels)
- Digital weighing balance
- Measuring cylinder
- Thermometer
- HPHT (High Pressure, High Temperature Filter Press Machine)
- Stop Watch

**Formulation of Mn<sub>3</sub>O<sub>4</sub>-based drilling fluid (Al-Yami and Nasr, 2007)**

ADDITIVES	FUNCTION	QUANTITY	
Deionized Water	Base	1928cm <sup>3</sup>	
Starch (Cassava Starch)	Fluid loss control agent	80g	
Potassium Chloride (KCl)	Density and shale inhibition	41g	
Potassium Hydroxide (KOH)	pH control	1g	
Calcium Hydroxide (Ca(OH) <sub>2</sub> )	Weighing material	0.5g	
Calcium Carbonate (CaCO <sub>3</sub> (Fine))	Weighing material	7g	
Calcium Carbonate (CaCO <sub>3</sub> (Medium))	Weighing material	3g	
Manganese Tetraoxide(Mn <sub>3</sub> O <sub>4</sub> )	Weighing material	400g	
Sodium Sulphide (Na <sub>2</sub> SO <sub>3</sub> )	Oxygen scavenger	1.5g	

**Filter Cake Creation Experiment**

HPHT (High Pressure High Temperature) filter press apparatus was used to create the filter cake formed by Mn<sub>3</sub>O<sub>4</sub>-based drilling fluids. The apparatus include cell, ending caps, ceramic disk, propeller, nitrogen gas line. A mud weighted by manganese tetraoxide was used in the formation of filter cake. The testing temperature and

pressure were set at 25°C and 100psi, respectively. During mud application, the bottom valve of the HPHT filter press machine was kept open to allow for filtrate leaking. The filtrate stopped at collected volume of 500ml. This indicates that an impermeable layer of filter cake has been formed on a metal disk. The cell was disassembled and the cake were removed from the cell for analysis where it was allowed to dried for 21 hours, its weight was measured to be 2500g, and its physical color was examined to be dark ash.

**HCl Soaking with the Filter Cake Created by Mn<sub>3</sub>O<sub>4</sub>-particles**

An amount of 40g of the created filter cake, each were soaked in various solutions of HCl (1-10 wt %) and reactions were allowed to proceed. The dissolution times were observed for various concentration of HCl and the times were recorded. This procedure was repeated at high temperatures (i.e. 60°C, 80°C, 110°C and 140°C). Results and Discussions

The results obtained in this investigation are presented as follows:

**Filter Cake Production**

The filter cake produced was 2500g or 2.5kg in weight and dark ash in color. This cake was used for the dissolution test in acid solution.

**Effect of HCl On Dissolution Of Mn<sub>3</sub>O<sub>4</sub>-particles At Ambient Temperature, As Well As at High Temperature Conditions**

The results obtained for the variation of dissolution of filter cake in HCl concentrations at different temperature is depicted in fig 1.

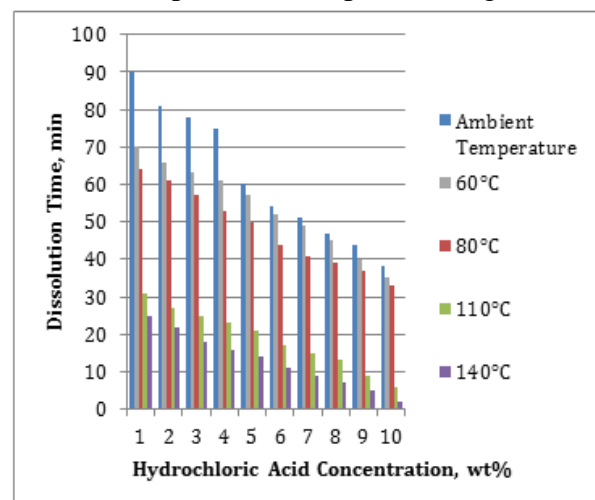


Fig: 1 Effect of HCl on Mn<sub>3</sub>O<sub>4</sub>-particles at different temperatures.

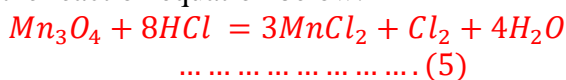
From Fig: 1, it could be seen that the dissolution time decreases with increasing temperature. This observation is in accordance with the general principles that dissolution time rate decreases with increasing temperature.

The experiment (HCl soaking with the filter cake) were conducted under ambient temperature as well as under high temperature conditions. This is collaborated by the fact that there is increase in temperature with depth while drilling.

Hydrochloric acid (1-10 wt%) dissolved 50% of the filter cake at ambient temperature, 70% at 60°C, 85% at 80°C, and 100% at 110°C, 140°C. The dissolution time of manganese tetraoxide increased with HCl acid concentration, and also increased with increasing temperature as shown in Fig. 1.

To carefully understand HCl/ Mn<sub>3</sub>O<sub>4</sub> reaction and select the appropriate HCl concentration, the reaction of 1-10 wt% HCl as described in the experimental section was examined. For the set of experiments, 40 grams of Mn<sub>3</sub>O<sub>4</sub> particles or filter cake were added to (1-10 wt %) HCl solutions at different temperatures conditions (25°C, 60°C, 80°C, 110°C, and 140°C) until the formation of effervescence stop, which indicate the completion of the reaction as shown in Fig. 1.

Releases of some gasses was noticed at 10 wt% HCl concentration at ambient temperature, 8-10 wt% HCl at 60°C, 7-10 wt% HCl at 80°C, 5-10 wt% HCl at 110°C and 4-10 wt% HCl at 140°C. This was noticed through the formation of bubbles. The gas should be chlorine gas based on the reaction equation below:



However, at 1-10 wt% HCl concentration no bubble was notice for 1hour 30 minutes. The formation of these gasses could be attributed to the released of chlorine gas and other gasses during the cause of reaction at elevated temperatures. Therefore, hydrochloric acid of concentration of 3 wt% is sufficient to dissolve most of the filter cake, without bubbling. HCl concentration above 3 wt% HCl is not recommended to prevent chlorine gas releases, most especially at high temperatures. The presence of chlorine gas is a major concern because it is a strong oxidizer, toxic and highly corrosive gas when dissolve in water.

Since the HCl consumed almost completely (1 – 40g Mn<sub>3</sub>O<sub>4</sub>), the reaction is irreversible which agrees with literature.

## CONCLUSION

In this study, the reaction of HCl was examined with manganese tetraoxide particles and Mn<sub>3</sub>O<sub>4</sub>-water based filter cake. Based on the results obtained, the following conclusions can be drawn:

At ambient temperature, only 10 wt% HCl concentration dissolved Mn<sub>3</sub>O<sub>4</sub> filter cake produced.

Reaction times were generally low at high temperatures compared to reaction times at low temperatures.

Above 3wt% HCl concentration, formation of chlorine gas was observed.

## RECOMMENDATIONS

HCl concentration above 3 wt% is not recommended (Especially at high temperature) because of the release of chlorine gas, which is corrosive and toxic.

HCl concentration below 10 wt% is not recommended (under ambient temperature) due to partial dissolution, which will result in formation damage.

End users of Mn<sub>3</sub>O<sub>4</sub> filter cake should be sensitized on the use of HCl concentrations compatible with best practices in the drilling industry.

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