REMOVAL OF FILTER CAKE GENERATED BY MANGANESE TETRAOXIDE WATER-BASED DRILLING FLUIDS

A Thesis

by

ABDULLAH MOHAMMED A. AL MOJIL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2010

Major Subject: Petroleum Engineering

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ABSTRACT

Removal of Filter Cake Generated by Manganese Tetraoxide
Water-based Drilling Fluids. (August 2010)
Abdullah Mohammed A. Al Mojil, B.S., King Fahd University of Petroleum and Minerals
Chair of Advisory Committee: Dr. Hisham A. Nasr-El-Din

Three effective solutions to dissolve the filter cake created by water-based drilling fluids weighted with Mn_3O_4 particles were developed. Hydrochloric acid at concentration lower than 5 wt% can dissolve most of Mn_3O_4-based filter cake. Dissolving the filter cake in two-stage treatment of enzyme and organic acid was effective and eliminated the associated drawbacks of using HCl. Finally, combining low and safe concentration of HCl with an organic acid in one-stage treatment was very effective.

Hydrochloric acid (10-wt%) dissolved 78 wt% of Mn_3O_4-based filter cake at 250°F after 28 hours soaking time. However, Chlorine gas was detected during the reaction of 5 to 15-wt% HCl with Mn_3O_4 particles. At 190°F, 1- and 4-wt% HCl dissolved most Mn_3O_4 particles (up to 70-wt% solubility). Their reactions with Mn_3O_4 particles followed Eq. 8 at 190°F, which further confirmed the absence of chlorine gas production at HCl concentrations lower than 5-wt%.

EDTA and DTPA at high pH (12) and acetic, propionic, butyric, and gluconic acids at low pH (3-5) showed very low solubilities of Mn_3O_4 particles. GLDA, citric, oxalic, and tartaric acids produced large amounts of white precipitation upon the reactions with Mn_3O_4 particles. Similarly, DTPA will produce damaging material if used to dissolve Mn_3O_4-based filter cake in sandstone formation.

At 4-wt% acid concentration, lactic, glycolic, and formic acids dissolved Mn_3O_4 particles up to 76 wt% solubility at 190°F. Malonic acid at lower concentration (2-wt%) dissolved 54 wt% of Mn_3O_4 particles at 190°F.

Manganese tetraoxide particles were covered with polymeric material (starch), which significantly reduced the solubility of filter cake in organic acids. Therefore, there was a need to remove Mn_3O_4-based filter cake in two-stage treatment. Enzyme-A (10-wt%) and Precursor of lactic acid (12.5-wt%) dissolved 84 wt% of the filter cake.

An innovative approach led to complete solubility of Mn_3O_4 particles when low and safe concentration of HCl (1-wt%) combined with 4-wt% lactic acid at 190°F. HCl (1-wt%) combined with lactic acid (4-wt%), dissolved 85 wt% of the Mn_3O_4-based filter cake after 18-22 hours soaking time at 250°F in one stage treatment.

DEDICATION

I dedicated this thesis to my parents.

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CHAPTER I

INTRODUCTION: THE IMPORTANCE OF RESEARCH

Weighting Materials in Drilling Fluids – Advantages and Limitations

Several advantages and limitations are associated with weighting materials used in drilling fluids, such as, bentonite, barite, calcium carbonate, ilmenite[1], manganese tetraoxide[2], and hematite[3]. Barite and bentonite are not soluble in HCl and therefore they may cause formation damage. Additionally, Because of the heavy metal components, including lead, cadmium, mercury and arsenic, associated with barite, it is considered one of the biggest potential sources of pollution. Portions of these heavy metals can be dissolved into the sea during the discharge of mud or cuttings (Rae et al. 2001). Barite also creates unwanted frictional pressure that results in excessive equivalent circulating density (ECD) (Ezell and Harrison 2008). Davies et al. (2009) evaluated a barite dissolver system but he did not show solubility results nor information about the chemistry of the system. The overall filter cake removal he used was costly that involved 4 stages of mutual solvent, $CaCO_3$ dissolver, and two barite dissolving treatments. To reduce the overall cost of the treatment he did not employ a coiled tubing technology. Some studies have proposed denser material in place of barite such as ilmenite. The heavy toxic metal content of ilmenite is significantly lower than that of barite (Rae et al. 2001; Amighi and Shahbazi 2010). However, ilmenite causes severe erosion problems and abrasiveness (Blomberg and Melberg 1984; Saasen et al. 2001). Additionally, the presence of iron oxide in ilmenite is a concern. Hematite will release a lot of iron if removed by HCl (ferric ions form insoluble hydroxide gels at relatively low pH values, about 1.5) (Morgenthaler et al. 2000). Other disadvantages of hematite include abrasiveness and higher sag tendency (Howard 1995). Moreover, hematite could result in severe slumping during static drilling conditions (Bern et al. 1998; 2000). The most commonly used acid soluble weighting material and bridging agent is $CaCO_3$. The specific gravity of $CaCO_3$ (2.71) limits its application when high density drilling fluids are needed to drill deep wells.

A high density and acid-soluble option is manganese tetraoxide (Mn_3O_4) (Bern et al. 1996). Mn_3O_4 is spherical in shape, has an average partial size of 1 micron, and specific gravity of 4.8. Svendsen et al. (1995) introduced manganese tetraoxide to potassium formate drilling fluid to

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This thesis follows the style of *SPE Journal*.

[1] Ilmenite is an oxide of iron and titanium with a chemical formula of $FeTiO_3$ or [FeO TiO_2] and specific gravity of 4.67.
[2] Manganese tetraoxide (or tetroxide) has a chemical formula of Mn_3O_4 and specific gravity of 4.8.
[3] Hematite or Haematite is an iron oxide with chemical formula Fe_2O_3.

increase its density to 106 lb/ft^3. Due to the partial solubility of barite in typical formate brines and the decision not to acidize these new wells, $CaCO_3$ and barite were not selected. The recommended cleaning fluid to remove the filter cake was 10-wt% citric acid dissolved in formate brine (Donovan and Jones 1995; Svendsen et al. 1995; Downs et al. 2005). The spherical shape of manganese tetraoxide reduces the particle-to-particle interactions which results in low plastic viscosity (PV) value. Mn_3O_4 also provides a low rheology fluid and equivalent anti-sag at lower cost (Kleverlaan and Lawless 2004; Carbajal et al. 2009). Tehrani et al. (2007) noticed that Mn_3O_4-based drilling fluid might undergo degree of flocculation and produced higher plastic viscosity value upon heat aging. To avoid aggloromation of Mn_3O_4 particles at high temperatures, Mu et al. (2006) suggested synthesizing Mn_3O_4 particles using H_2O_2 as an oxidant and starch as a capping agent. Starch is used as dispersant in the synthesis of single-phase, spherical, uniformly dispersive Mn_3O_4 nanoparticles (Mu et al. 2006). Also, development of dispersant package for available commercial manganese tetraoxide particles in water and oil-based muds would minimize the aggloromation problem.

Mn_3O_4 was introduced as a weighting material to oil-based drilling fluids because of the low plastic viscosity of the mud, the fluid density requirement, and the ability of the mud to suspend Mn_3O_4 particles at a lower fluid viscosity (Oakley et al. 2000; Franks and Marshall 2004). Oil-based muds weighted with Mn_3O_4 enhanced the rate of penetration in Crab Orchard Sandstone formation by 100% (Black et al. 2008). Gregoire et al. (2009) used a blend of $BaSO_4$ and Mn_3O_4 particles in Oil based muds. Murphy et al. (2008) published procedure to determine dynamic sag in water-based and oil-based muds that are weighted with manganese tetraoxide particles.

Al-Yami developed a water-based drilling fluid weighted with manganese tetraoxide and a small amount of $CaCO_3$ particles at improved rheological properties. $CaCO_3$ was used to control drilling fluid leak-off rate (Al-Yami and Nasr-El-Din 2007). Manganese tetraoxide were also employed as a weighting material for cement-drilling fluid spacer, packer, invert emulsions, cementing, and other completion fluids (Svendsen et al. 1998; Pine et al. 2003; Bland et al. 2006; Steele and Hart 2007; Moroni et al. 2008; Eldin et al. 2009). North and Frittella noted that Mn_3O_4 provides excellent weighting, high temperature suspension properties, and enhanced stability of cement slurries. Mn_3O_4 can be added directly to the mix water before the cement is added, reducing the time that the mixed slurry has to be held on surface (North et al. 2000; Frittella et al. 2009).

Formation Damage by Mn_3O_4-Drilling Fluids

Al-Yami et al. (2008) determined formation damage induced by three different muds of the same density (95 lb/ft^3). The results indicated that drilling mud weighted by Mn_3O_4 particles caused less damage than formate or barite/calcium carbonate-based mud. He also compared formation damage resulted from solids invasion in various drilling fluids including Mn_3O_4-based muds (Al-Yami et al. 2010). However, Mn_3O_4 particles aggregate up to 20 microns in aqueous and oil-based fluids (Svendsen et al. 1995; Tehrani et al. 2007). Accumulation of these aggregates in the critical near wellbore area is not desirable, and can result in stuck pipe during drilling operations. Howard noted a possibility of dust problems that could cause formation damage (Howard 1995). Additionally, we noticed in this study that starch present in the filter cake covered Mn_3O_4 particles which resulted in additional particles aggloromation. Thus, addressing the removal of filter cake formed by drilling fluid weighted with Mn_3O_4 particles is essential to ensure the effectiveness of the drilling and cleaning operations. In 2008, we published the first study that addresses the removal Mn_3O_4-based drilling (Al Moajil et al. 2008).

Filter Cake Removal Techniques

Several cleaning fluids were used to remove filter cake which include: live HCl acid, gelled acids, organic acids, chelating agents, oxidizing agents, enzymes, *in-situ* generated organic acids, microemulsions, or a combinations of these chemicals (Rickards et al. 1993; Morgenthaler et al. 1998; Stanley et al. 1999; Brady et al. 2000; Morgenthaler et al. 2000; Rae et al. 2001; Parlar et al. 2002; Abiodun et al. 2003; Ali et al. 2004; Downs et al. 2005; Leschi et al. 2006; Al Moajil and Nasr-El-Din 2007; Nasr-El-Din et al. 2007; Al Moajil et al. 2008; Carrera and Ferreira 2009; Quintero et al. 2009; Marquez and Lenz 2010).

Removing the filter cake generated by water-based mud that contained Mn_3O_4 is a difficult task. Unlike other weighting materials, Mn_3O_4 has tetragonal symmetry, nonstoichiometry behavior (locally composed of a tetrahedral MnO phase and octahedral Mn_2O_3 phase), and it is a strong oxidizing agent (Chern et al. 2000; Gillot et al. 2001; Berbenni and Marini 2003; Marbán et al. 2004; Peña et al. 2007; Al Moajil et al. 2008; Zhao et al. 2009). Thus, dissolving Mn_3O_4-based filter cake involves many interactions and challenges as well be discussed in the following sections.

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 valances 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_3O_4, Mn_5O_8, Mn_2O_3, MnO_2, and Mn_2O_7. All hydroxides and oxides of manganese form Mn_3O_4 when heated to 1,000°C (Kemmitt and Peacock 1973). Mn_3O_4 forms in nature as the mineral hausmannite (Weiss 1977). Hausmannite [Mn_3O_4 or $(Mn^{2+})(Mn^{3+})_2O_4$], a distorted spinel oxide mineral with Mn^{2+} in tetrahedral coordination and Mn^{3+} in distorted octahedral coordination, is a metastable intermediate in the oxidation of soluble Mn(II) to form thermodynamically-stable MnO_2 (Peña et al. 2007). Particle size and temperature affect the oxidation properties of Mn_3O_4. Using thermal gravimetric technique (TGA), Gillot studied the effect of particle size of Mn_3O_4 particles on the oxidation to α-Mn_2O_3. He noticed that at low heating rate (3°C/hr) and small particle size, two metastable manganese oxides exist, a cation deficient spinel (Mn_2O_2) with Mn^{2+} ions oxidation and Mn_5O_8 associated to Mn^{3+} ions oxidation (Gillot et al. 2001). Mn_3O_4 has been proposed as a cheap, environment-friendly catalyst for the oxidation of CH_4, corrosion-inhibiting pigment for epoxypolyamide, and in top coating applications (Mu et al. 2006).

Reactions of Manganese Oxides With Acids and Chelating Agents

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:

$$Mn_3O_4 + 8HCl \rightleftharpoons 2MnCl_2 + MnCl_4 + 4H_2O \text{ .... (1)}$$

$$3Mn_3O_4 + 12HCl \rightleftharpoons 6MnCl_2 + 3MnO_2 + 6H_2O \text{ .... (2)}$$

$$Mn_2O_3 + 6HCl \rightleftharpoons MnCl_2 + MnCl_4 + 3H_2O \text{ .... (3)}$$

$MnCl_4$ will decompose and give $MnCl_2$ and poisons/corrosive chlorine gas. Therefore, as reported by Depourdeaux (1904), Eq.3 becomes:

$$Mn_3O_4 + 8HCl \rightleftharpoons 3MnCl_2 + Cl_2 + 4H_2O \text{ .... (4)}$$

Moreover, in acidic solutions Mn_3O_4 associate with dissolved chlorine as $(Mn_3O_4Cl_2)^{2+}$ 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_3O_4 with cleaning fluids could be due to the tetragonal symmetry of Mn_3O_4 (Chern et al. 2000). Fe_3O_4 and Mn_3O_4 have similar crystalline structure but different curie temperatures, 858 and 43°K respectively. Therefore, magnetization of Mn_3O_4 decreases with temperature (Chern et al. 2000).

Treatment of Mn(II) carbonate with hydrofluoric (HF) acid produces a sparingly soluble MnF_2 in water (Kemmitt and Peacock 1973). Hydrofluoric acid is not used in carbonate formations because of precipitation of calcium fluoride. In sandstone formations, the use of HF acid requires certain preflushes, and various additives to minimize the impact of secondary and tertiary reactions. In both formations, HF acids cannot be used to remove Mn_3O_4.

A general agreement exist that, although MnO_2 phases are the favored secondary precipitates at low pH (Eq. 2), conversion to manganite (γ-MnOOH), is favored at pH 4 (Eqs. 4 and 5) (Peña et al. 2007). Hem and Lind (1983) proposed a two-step cyclic sequence for this latter reaction: The first step is the protonation of hausmannite to form manganite, while the second step is the oxidation of soluble Mn(II) released in the first step to reconstitute hausmannite and thereby buffer the soluble Mn(II) (Peña et al. 2007).

$$Mn_3O_4(s) + 2H^+ \rightleftharpoons Mn^{+2} + 2\gamma\text{-}MnOOH(s) \text{ .... (5)}$$

$$Mn^{+2} + 1/_6O_2(g) + H_2O(l) \rightleftharpoons 1/_3Mn_3O_4(s) + 2H^+ \text{ .... (6)}$$

In biologically-active systems, organic ligands strongly influence the weathering of manganese oxides. For example, the transformation of hausmannite to manganite at circumneutral pH is significantly slowed by the presence of oxalate, a common biotic ligand, as a result of a sorbed Mn-oxalate layer which likely hinders surface-controlled reactions (Peña et al. 2007). Thus, selection of pH is very important in the dissolution of Mn_3O_4. For instance, we found in this study that the reaction of ethylene diamine tetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) is slow at high pH, while the reaction rate of dicarboxymethyl glutamic acid (GLDA) is very rapid at low pH as will be shown later.

Manganese forms different salts with organic acids. Many manganese salts of mono and dibasic carboxylic acids are known and compounds of Mn (II), (III), and (IV) exist. The stability constants of wide variety of organic acids with Mn(II) and Mn(III) are determined by Kemmitt and Peacock (1973). Manganese acetate is available as manganese (III) acetate dihydrate $[Mn(CH_3COO)_3.2H_2O]$, manganese (IV) acetate $[Mn(CH_3COO)_4]$, and Mn(II) acetate $[Mn(CH_3COO)_2.4H_2O)]$ (Arndt 1981; Moses Ezhil Raj et al. 2009). Mn(III) can be present in strong acidic solutions in the presence of excess Mn(II) (Arndt 1981). The reactions of acetic acid and with Mn_3O_4 (Eq. 7) produces Mn(II) acetate (Patnaik 2003).

$$Mn_3O_4 + 2CH_3COOH \rightleftharpoons Mn(CH_3COO)_2 + Mn_2O_3 + H_2O \quad \text{........................} \ (7)$$

The red monoclinic crystals of Mn(II) formate dehydrate $[Mn(OCOH)_2.2H_2O]$ are obtained by the reaction of formic acid with $MnCO_3$. Mn(III) formate $[Mn_3(OCOH)_6(OCOH)_3.2H_2O]$ is prepared by the reaction of formic acid with MnO_2 (Kemmitt and Peacock 1973). Three manganese citrates have been reported $[Mn_3(C_6H_5O_7)_2$, $Mn(C_6H_6O_7).H_2O$, and $Mn_3(C_6H_5O_7)_2.10H_2O]$. The formation of these salts depends on the stoichiometry of manganese oxides to citric acid (Kemmitt et al. 2001; Hawley et al. 2002). The following reported manganese lactate is used in medicine: $[CH_3CH(OH)COO]_2Mn.H_2O$ (Weiss 1977).

The rate of reaction of manganese oxides with organic acids depends on the structure of the acid, the ability of the chelate function in the acid, and the stoichiometry of the reactants (Kemmitt et al. 2001). In the case of acetic acid, there is no secondary function able to chelate. Therefore, the solubility of Mn_3O_4 in acetic acid is low. α-hydroxy monoacids (glycolic and lactic) react more slowly than diacids. The reaction of diacids depends on the resulting chelate ring size, thus oxalic acid (5-mebered ring) is the fastest, followed by malonic (6-mebered ring) and so on. Malic and tartaric acids contain α-hydroxyls and form complexes analogous to lactic and glycolic acids, and their reaction rate is close to diacids (Kemmitt et al. 2001). However, a common problem with organic acids is the precipitation of damaging material which should be considered carefully in acid selection.

Mn(II) forms a variety of chelates such as $Mn(EDTA)^{-2}$ which has an equilibrium constant of 13.4. Peña et al. (2007) examined the dissolution of Mn_3O_4 using desferrioxamine B (DFOB)[4], a trihydroxamate siderophore, at different pH ranges. He reported four reaction mechanisms, the dominant mechanism depend on pH. For example, above pH 8, a non-reductive ligand-promoted

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[4] The form of DFOB utilized in Peña study is the mesylate salt $[C_{25}H_{46}N_5O_8NH_3^+(CH_3SO_3)^-]$ produced under the trade name Desferal. The siderophore desferrioxamine B (DFOB) has a linear molecular structure with three hydroxamate moieties and a terminal amine group.

dissolution dominated, whereas below pH 8, the dissolution was non-stoichiometric with respect to DFOB. As pH decrease, the release of manganese ions either by reductive or induced dissolution increases linearly. He also found that DFOB have more affinity to Mn^{+3} than Fe^{+3}.

Marbán et al. (2004) studied the catalytic properties of Mn_3O_4 involved in the reduction of nitrogen oxide (NO) with surface active NH_3. In this study, manganese tetraoxide employed as a catalyst due to its active phase, a nonstoichiometric Mn_3O_4 locally composed of an octahedral Mn_2O_3 phase and a tetrahedral MnO phase. Thus, two mechanisms involved in the reduction of NO due to both the octahedral (oxygen vacancies) and tetrahedral (oxygen excess) environments of Mn_3O_4. The latter initially accounts for 60% of the total NO reduction. Aminooxy groups formed on the locally octahedral environment of Mn_3O_4 (Mn_2O_3) react with gaseous NO_2 followed by surface catalytic reaction by ammonium ions on the locally tetrahedral environment of Mn_3O_4 (MnO). At 125°C gas-phase oxygen cannot dissociate on the oxygen vacancies of the octahedral environment, but can partly oxidize the tetrahedral MnO phase (Marbán et al. 2004). Zhao et al. (2009) employed Mn_3O_4 as a catalyst to accelerate the chelation reaction of molybdenum from $MnSO_4$.

As can be seen, the reaction of acids and chelating agents with manganese oxides is complex. Some of the reaction products have low solubility in water (**Table 1**) and can cause formation damage. Extensive lab testing is needed before selecting the cleaning fluid that can be used to remove filter cake formed by Mn_3O_4.

TABLE 1—SOLUBILITY AND CHEMICAL FORMULA OF SELECTED MANGANESE SALTS

Mn(Salt)	Formula	Color -Crystal	Solubility	Reference
Mn(VI) acetate	$Mn(CH_3COO)_4$	-	-	Arndt 1981
Mn(III) acetate	$Mn(CH_3COO)_3.2H_2O$	-	-	Arndt 1981
Mn(II) acetate	$Mn(CH_3COO)_2.4H2O$	-	38 g/100 ml 65 g/100 ml at 50°C	Linke 1965; Perry 1998; Dean 1999
Mn(II) formate	$Mn(OCOH)_2.2H_2O$	red monoclinic Octahedral	-	Kemmitt and Peacock 1973
Mn(II) lactate	$Mn(CH_3CHOHCOO)_2.2H_2O$	pink monoclinic	10 g/100 ml	Manganese Lactate Purified Crystals
Mn(II) lactate	$Mn(CH_3CHOHCOO)_2.3H_2O$	red crystals	-	Kemmitt et al. 2001
Mn(III) citrate	$Mn_3(C_6H_5O_7)_2$	-	-	Hawley et al. 2002
Mn(III) citrate	$Mn(C_6H_5O_7).H_2O$	-	-	Kemmitt et al. 2001
Mn(III) citrate	$Mn_3(C_6H_5O_7)_2.10H_2O$	White powder	Water insoluble	Kemmitt et al. 2001
Mn(II) EDTA	-	-	-	Schuman 1971
Mn(II) EDTA	$MnNa_2EDTA$	-	120 g/100 ml at 80°C	Multi-Micro Mn-EDTA 2010
Mn(II) chloride	$MnCl_2.4H_2O$	-	143 g/100ml	Dean 1999
Mn(II) chloride	$MnCl_2$	Hexagonal	63.4 g/100 g at 0°C 73.9 g/100 g at 20°C 115 g/100 g at 100°C	Schuman 1971
Mn(VI) chloride	$MnCl_4$	Rose, monoclinic	soluble	Perry 1998

CHAPTER II

EXPERIMENTAL METHODOLOGY

Materials

Most chemicals were received from Sigma-Aldrich include hydrochloric acid (36.4 wt% by titration), dark red-brown manganese tetraoxide (> 90% Mn_3O_4) with a specific gravity of 4.8 and mean spherical particle size of 1 micron, Lactic acid (85 wt%), sodium hydroxide (NaOH) pellets manufactured by MallincKrodt Chemicals, phenolphthalein solution, potassium iodide manufactured by EM Science, and iodine solution. **Table 2** gives the concentrations of Mn_3O_4 as determined by X-ray fluorescence (XRF). NaOH was used in acid/base titration and phenolphthalein was used in both acid/base titration and chlorine gas analysis.

TABLE 2—ELEMENTAL ANALYSIS OF Mn_3O_4 AND $CaCO_3$ PARTICLES USING EDXRF[5]

Element		Mn	Ca	Fe	Zn	Pb	K	Si	Al	Mg	Ba	Sr
Mn_3O_4	**wt%**	**74.3**	**< 0.001**	**2.5**	**0.3**	**0.2**	**0.1**	**0.1**	**< 0.001**	**-**	**-**	**-**
$CaCO_3$-Fine	**wt%**	**-**	**36.3**	**0.1**	**-**	**-**	**-**	**0.8**	**0.2**	**0.4**	**< 0.001**	**0.2**
$CaCO_3$-Medium	**wt%**	**-**	**38.9**	**< 0.001**	**-**	**-**	**-**	**0.2**	**0.1**	**0.3**	**0.1**	**0.1**

Water-based drilling fluids weighted mainly with Mn_3O_4 and small amount of $CaCO_3$ particles to control leak-off rate were prepared in the lab (**Table 3**). We added xanthan, starch, and polyanionic cellulose (PAC-R) polymers to the mud to control fluid loss and rheological properties of the drilling fluid. The function of lime ($Ca(OH)_2$) and potassium hydroxide (KOH) is to adjust the pH of the drilling fluid. Sodium sulfite (Na_2SO_3) was added as an oxygen scavenger. **Table 4** summarizes the main properties of this mud.

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[5] Carbon and oxygen cannot be detected using this technique.

TABLE 3—FORMULATION OF DRILL-IN FLUID

Additive	Function	Amount added			
		Lab units (per ~320 cm^3)		Field unit (per bbl)	
		Quantity	Unit	Quantity	Unit
DI Water	Base	287.7	cm^3	0.822	bbl
Xanthan	Viscosifier	1	g	1	lb
Starch	Fluid loss control agent	6	g	6	lb
PAC-R[6]	Viscosifier/fluid loss	0.75	g	0.75	lb
KCl	Density and shale inhibition	41	g	41	lb
KOH	pH control	0.5	g	0.5	lb
$Ca(OH)_2$	pH control	0.25	g	0.25	lb
$CaCO_3$ (Fine)	Weighting material	3.5	g	3.5	lb
$CaCO_3$ (Medium)	Weighting material	1.5	g	1.5	lb
Mn_3O_4	Weighting material	202	g	202	lb
Na_2SO_3	Oxygen scavenger	0.75	g	0.75	lb

TABLE 4—PROPERTIES OF Mn_3O_4 DRILL-IN FLUID

Property	Conditions	Unit	Value
Density	80°F and 14.7 psi	lb/ft^3	95
Plastic viscosity	120°F and 14.7 psi	cp	27
Yield point		$lb/100\ ft^2$	38
API filtrate	Static at 75°F and 100 psi	cm^3/30 min	6.5
Cake thickness		in	1/32
HPHT filtrate	Dynamic at 250°F and 200 psi 3 µm, 400 md ceramic disc	cm^3/30 min	13.6-20.3
Cake thickness		in	0.24-0.29
pH	-	-	10-11

Filter Cake Removal Experiments

We used an HP/HT filter press apparatus to create the filter cake and determine effectiveness of cleaning fluids to remove the filter cake formed by the Mn_3O_4-based drilling fluids (**Fig. 1**). The apparatus included 500-cm^3 cell, ending caps, ceramic disks (permeability = 400 md and average pore size = 3 µm), a propeller, and nitrogen gas line. Each experiment was divided into four main steps: Brine discharge, generation of the filter cake, Cleaning fluid soaking with the filter cake (100- or 300-cm^3 solution), and final brine discharge test. The objective of the brine discharge tests was to measure the difference in brine flow rates before/after dissolving the filter cake. The filter cake was formed on a ceramic disc after 30 minutes filtration of the drilling fluid

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[6] PAC = Polyanionic cellulose

under dynamic conditions (~ 120 RPM). The filtrate volume was measured as a function of time. In most of the cases, cleaning fluid step was under static conditions at 250-300°F and 250 psi. The remaining solids after reaction were analyzed using XRD/XRF techniques.

Fig. 1—Dynamic HP/HT filter press

HP/HT Visual Cells and Analysis of Gases

Solubility tests of Mn_3O_4 particles in cleaning fluids were conducted using a HP/HT see-through-cell. The visual cell had a volume of 100 cm^3. Nitrogen gas was connected to the instrument and the cell was heated electrically by a silicone heater plates attached to the cell. Finally, the cell was covered with a jacket to maintain its temperature (**Fig. 2**). The tests conducted by mixing 5 g of Mn_3O_4 in 80-cm^3 cleaning solution. The soaking time was 24 hours at temperatures of 212 and 248°F. The cell was pressurized using nitrogen gas up to 250 psi. In addition to measure the solubility, we connected a small cylinder to the visual cell and flushed it with nitrogen gas. Then, we loaded the cell with the cleaning fluids and Mn_3O_4 particles and left them for a specified period of time. After the test, the valve to the small sampling cylinder was opened and, as a result, the pressure in the cell decreased and the pressure in the small cylinder increased. Finally, we analyzed the gas in the cylinder using gas chromatography/mass spectrometry (GC/MS) technique. More details on the procedure used for gas sampling from the visual cell were given by Al-Muntasheri et al. (2008). The remaining solids after reaction were analyzed using XRD/XRF techniques.

Fig. 2—HP/HT visual cell

Reaction Kinetics Experiments

In this study we examined the reaction of HCl, several organic acids, and chelating agents with manganese tetraoxide at 190°F under magnetic stirring and weight ratio of acid solution to Mn_3O_4 was 50:1 (4 g Mn_3O_4/200 g acid solution). During each experiment, we collected samples at different times and filtered each immediately through 0.2-micron Whatman syringe filter. Then we measured acid/chelating agent concentration through acid/base titration and manganese ions using flame atomic absorption spectroscopy (FAAS) (AAnalyst 700-flame type).

In HCl experiments, the association of Mn_3O_4 and chlorine is reported as $(Mn_3O_4Cl_2)^{2+}$ ions in acidic solutions (Auger et al. 1991). Chlorine is partially soluble in water. Measuring HCl concentration, and using phenolphthalein as an indicator, we noticed a disappearance of the pink color corresponding to the end point. This is because phenolphthalein was oxidized by chlorine. Therefore, we measured HCl concentration via an auto-titrator (end point at pH = 7).

The experimental setup appears as **Fig. 3**. Three observations were noted during the analysis of gases produced (if any) for each experiment. The gases were first bubbled in deionized (DI) water (Fig. 3). Then, we added a few drops of phenolphthalein to the DI water to notice any interactions with produced chlorine gas in case of HCl experiments. Third, the DI water pH value was measured before/after gas bubbling to note any decrease in pH value caused by the produced gases. The remaining solids after reaction were analyzed using XRD.

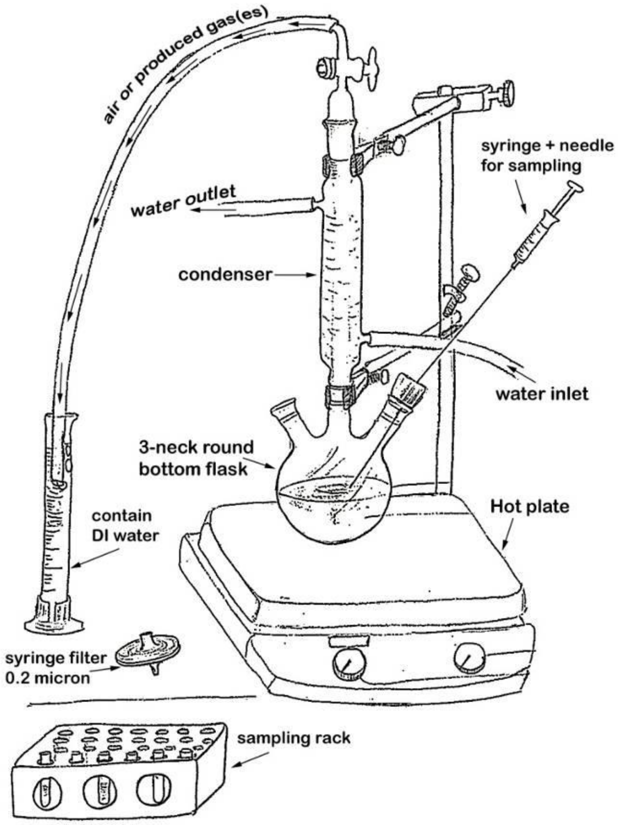


Fig. 3—Setup used to measure solubility of Mn_3O_4 particles in cleaning solutions

CHAPTER III

RESULTS AND DISCUSSION

Various organic acids (**Fig. 4**) and chelating agents (**Fig. 5**) in addition to hydrochloric acid were tested in this study. These include simple organic acids such as formic acid. α-Hydroxy acids such as glycolic acid which has chelation ability. Other organic acids include acid precursors, multi-hydroxy acids, and diacids. The chelating agents tested were amino carboxylic acids based on acetic acid where the main difference between them is the number of nitrogen atoms. The acids and chelating agents were selected based on the recommended fluids in the petroleum industry to dissolve filter cake and specifically the recommended acids to dissolve manganese oxides in other industries such as the study conducted by Kemmitt et al. (2001). As explained earlier Kemmitt et al. (2001) noted three factors that affect the reaction of manganese oxides with organic acids, the structure of the acid, the ability to chelate in the acid, and the reactants stoichiometry.

The results indicated high solubility of the filter cake using HCl acid at high concentrations. However, high HCl concentrations are risky because of chlorine gas production. Lower concentrations dissolved safely most of Mn_3O_4 particles.

Some acids were weak with Mn_3O_4 and others produced damaging material upon the reaction with Mn_3O_4. The third group of acids dissolved Mn_3O_4 particles effectively. These acids alone dissolved most of Mn_3O_4 particles but not Mn_3O_4-based filter cake because of the polymers present in the filter cake (mainly, starch).

Treating Mn_3O_4-based filter cake in two-stage treatment of enzyme and organic acid stages improved the solubility of the filter cake up to 85-wt% depending on the acid selected and concentrations of the enzyme and the acid. This is because polymeric constituents covered manganese tetraoxide particles which need to be removed first.

Combining an organic acid with HCl at lower and safe concentration, dissolved Mn_3O_4 particles completely and 85 wt% of the Mn_3O_4 filter cake. Increasing the acids concentrations would increase the solubility of the filter cake.

Therefore, we proposed three solutions to dissolve the filter cake created by Mn_3O_4-based drilling fluids. An engineer can decide on the proper method to dissolve Mn_3O_4-based filter cake depending on the available options that he has. For example, if he can use HCl or not and at what maximum concentration. The treatment cost and time are other factors to select the optimal solution to dissolve Mn_3O_4-based filter cake. Finally, if a complete removal of the filter cake is not desirable or filter cake disturbance is sufficient to eliminates the drawback of damage created then a different solution can be implemented.

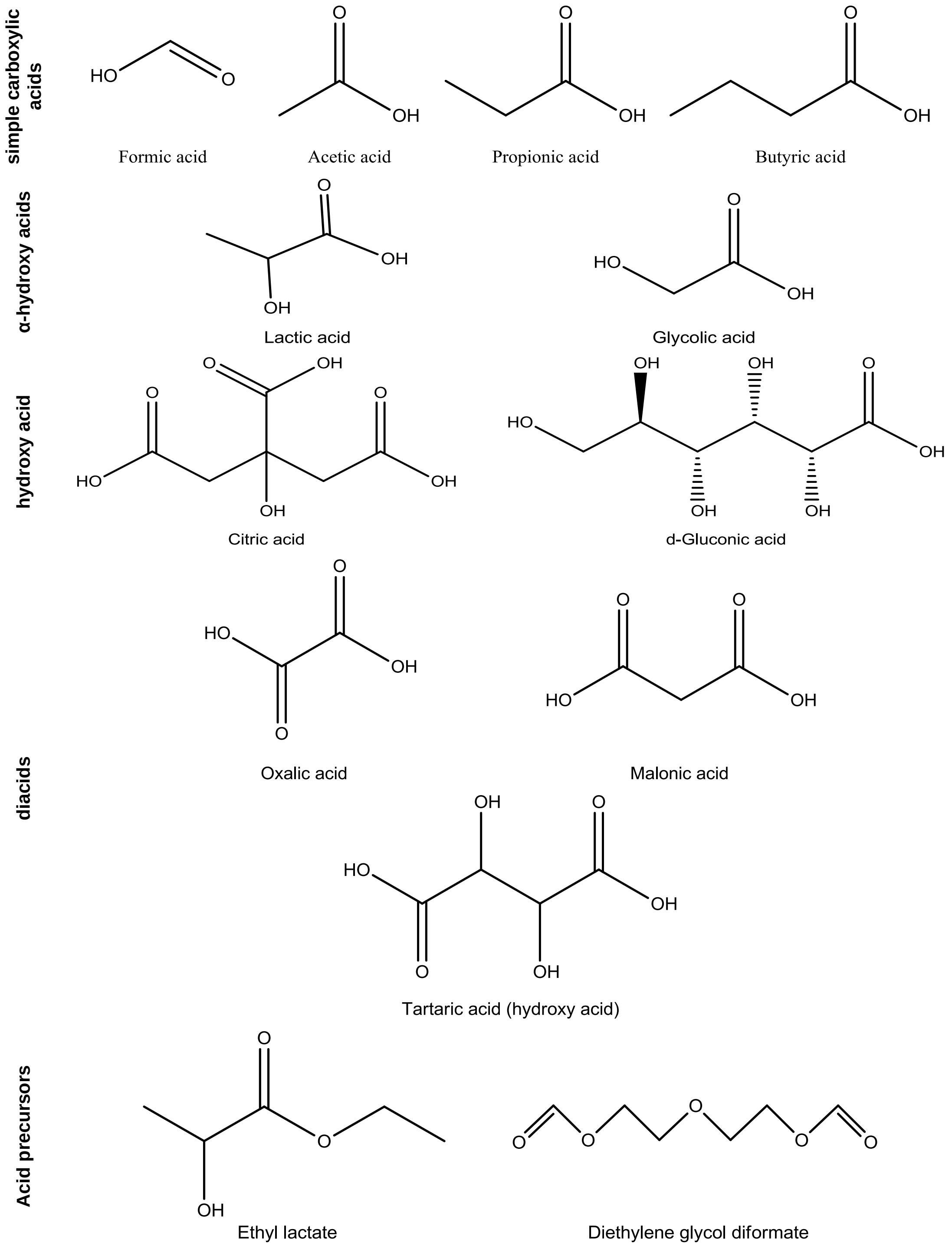
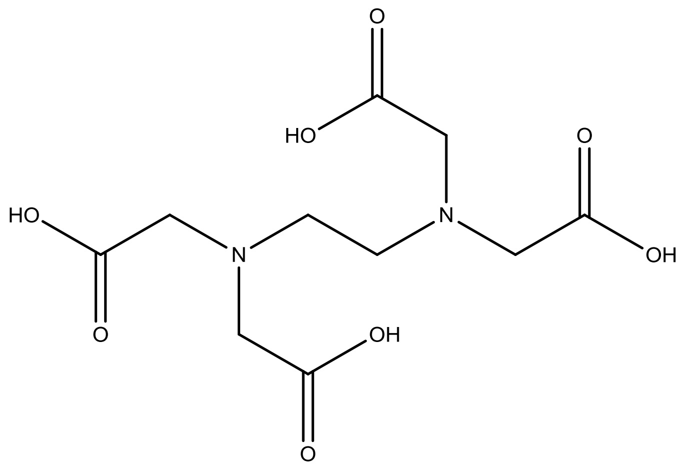
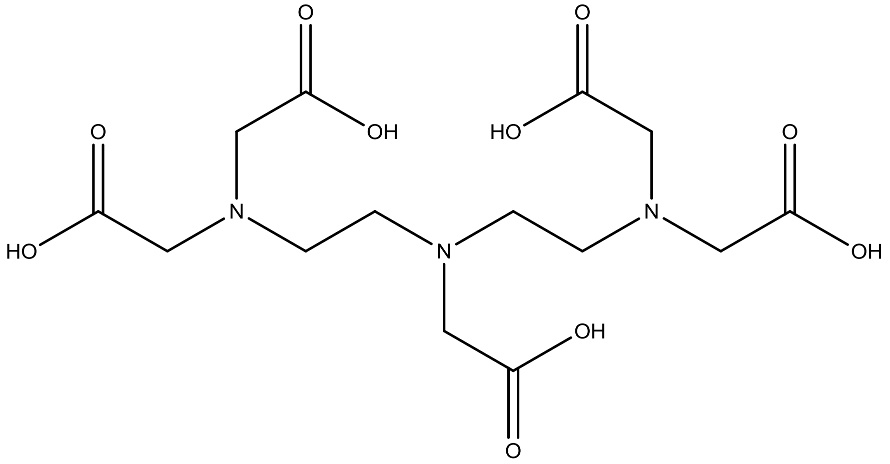


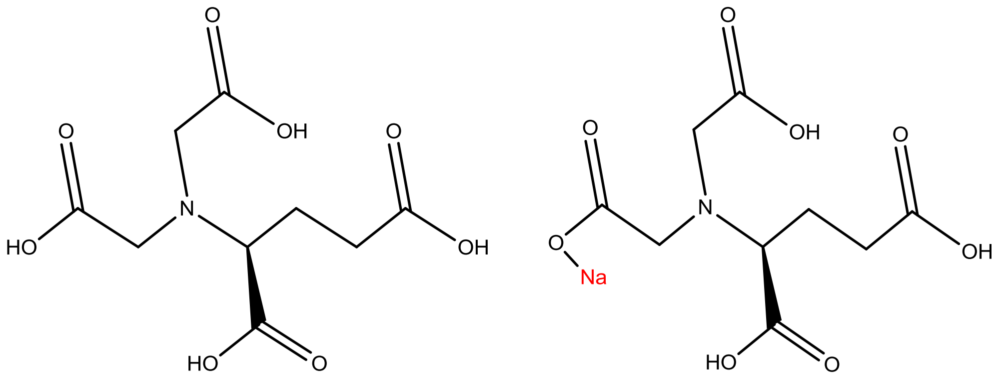
Fig. 4—Chemical structure of selected organic acids and their precursors



Ethylene diamine tetraacetic acid (EDTA)



Diethylene triamine pentaacetic acid (DTPA)



l-Glutamic acid, N, N-diacetic acid (H4-GLDA)
pH = 1.7

H3-GLDA
pH = 3

Fig. 5—Chemical structure of chelating agents

Reaction of Hydrochloric Acid With Mn_3O_4-Based Filter Cake

Solubility of Mn_3O_4 Particles and Filter Cake in HCl

To examine the efficiency of HCl to dissolve the filter cake, we used a HP/HT filter press first as described earlier. Hydrochloric acid (10-wt%) dissolved 78 wt% of the filter cake at 250°F, 250 psi, and 28 hours soaking time (**Fig. 6**). Therefore, Hydrochloric acid hydrolyzed biopolymers present in the filter cake and dissolved Mn_3O_4 and $CaCO_3$ particles. We should note that during HCl soaking step, HCl was not mixed with the filter cake.

Fig. 6—Mud cakes before/after the reaction of 10 wt% HCl with Mn_3O_4-based filter cake, P = 250 psi, T = 250°F, and soaking time = 28 hours

Solubility tests were conducted on Mn_3O_4 particles as received using visual cell apparatus. We soaked 5 g of Mn_3O_4 particles in 80-cm^3 HCl solutions. Hydrochloric acid concentrations were 5-, 10-, and 15-wt% at 212 and 284°F. The solubility of manganese tetraoxide increased with acid concentration and temperature (**Fig. 7**). During HCl reaction with Mn_3O_4 particles or filter cake, the solutions were not mixed. Obviously, keeping the reactants mixed during the reaction would result in higher solubilities.

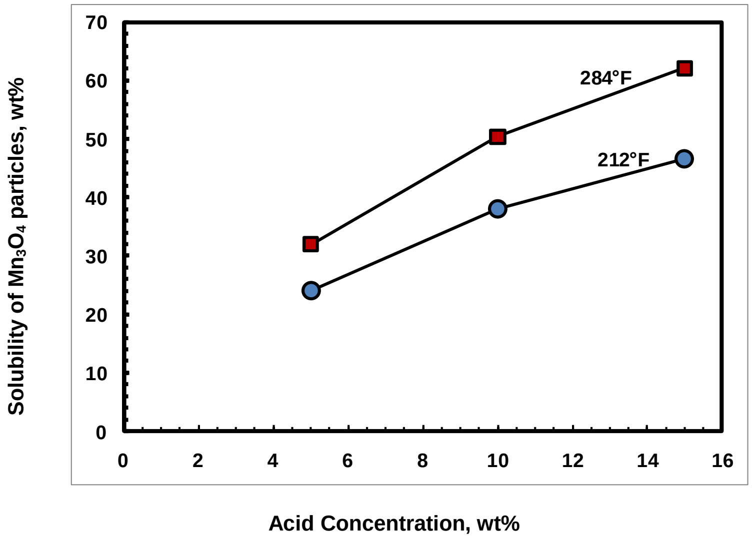


Fig. 7—High temperatures consistently increased solubility of Mn_3O_4 particles in HCl w/o mixing, visual cell apparatus

Reaction of Mn_3O_4 Particles With Hydrochloric Acid

To carefully understand the HCl/Mn_3O_4 reaction and select the appropriate HCl concentration, we examined the reaction of 1-, 4-, and 10-wt% HCl as described in the experimental section. Four grams of Mn_3O_4 particles were added to 200 grams of HCl solutions at temperature of 190°F under magnetic stirring until the reaction reached completion. We collected samples at different times to measure HCl and manganese concentrations (using atomic absorption).

The results indicated different reaction products at 10-wt% HCl than 1- and 4- wt% HCl. The reaction of Mn_3O_4 with 10-wt% HCl results in water-soluble reaction products (manganese chlorides), while at 1- and 4-wt% HCl, the reactions produce both water-soluble and insoluble products (manganese chloride and oxide]. Thus, 10 wt% HCl dissolved 100 % of Mn_3O_4 particles while the solubility decreased to 56- and 70-wt% at 1- and 4-wt% HCl, respectively (**Table 5**).

TABLE 5—SOLUBILITY OF Mn_3O_4 PARTICLES IN HCl ACID SOLUTIONS, 190°F

HCl Concentration, wt%	Dissolved solids, wt%	Weight of retained solids after reaction, g	Manganese Concentration, mg/l
1	56	1.76	~ 7,500
4	70	1.2	~ 8,500
10	100	0	~ 18,000

Manganese concentrations in spent HCl solutions as a function time (**Fig. 8**) indicated higher reaction rate at 10-wt% HCl than 1- and 4- wt% HCl. The reaction time until completion was less than 3 minutes when 10-wt% HCl used while it was more than 6 minutes at 1- and 4-wt% HCl. Fig. 8 indicated total solubility of Mn_3O_4 particles at 10 wt% HCl (4 grams ≡ 17,400 to 17,900 mg/l, calculated). In case of 1- and 4-wt% HCl, the maximum Mn concentration was in the range of 7,500 to 8,500 mg/l (Table 5 and Fig. 8).

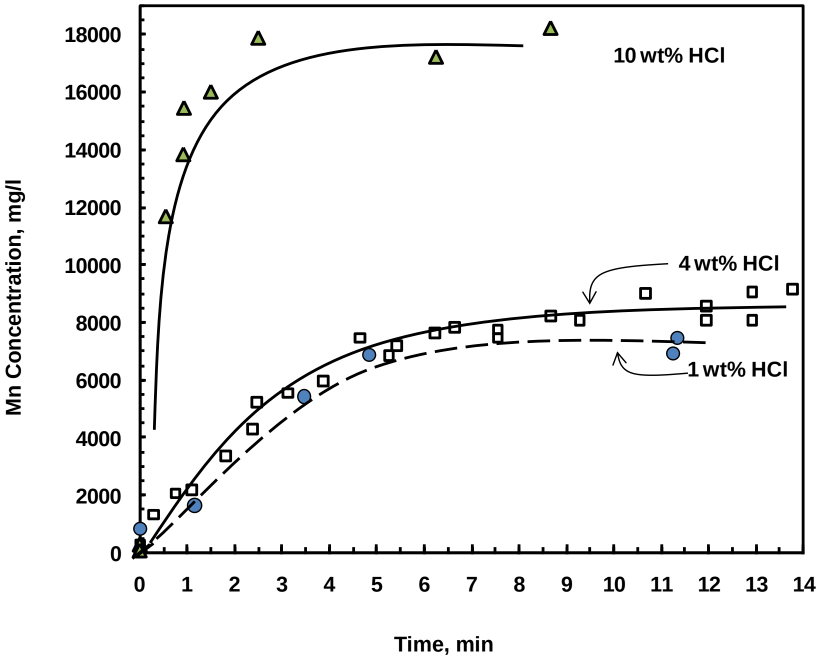


Fig. 8—Effect of HCl concentration on the dissolution of manganese ions, 190°F

Fig. 9 showed 88 % of acid concentration consumed at 1-wt% HCl, which indicate that the reaction stoichiometry is about 1-wt% HCl at 190°F. At HCl concentrations of 4- and 10-wt%, HCl consumptions were 25 and 20 %, respectively. Gases released from the reactions (if any) were bubbled into DI water where pH was measured before and after gases release. We noticed release of chlorine gas only at 10-wt% HCl through bubbles. Also, the results indicated decrease in the pH of the DI water by 2 to 3 units (**Table 6**). The decrease in pH value can be explained by the release of acid gases and volatility of HCl. In addition, phenolphthalein was oxidized when added to the DI water at only 10 wt% HCl. We arrived at this conclusion because the pink color of the DI water after addition of phenolphthalein disappeared and was not recovered when we increased the pH by adding NaOH indicating the presence of dissolved chlorine gas. Additionally, Acid/base titration of spent HCl (10-wt% initial concentration) solutions resulted in less accurate measurements when phenolphthalein is used as indicator. Thus, we used auto-titrator apparatus to measure HCl concentration (pH set at 7).

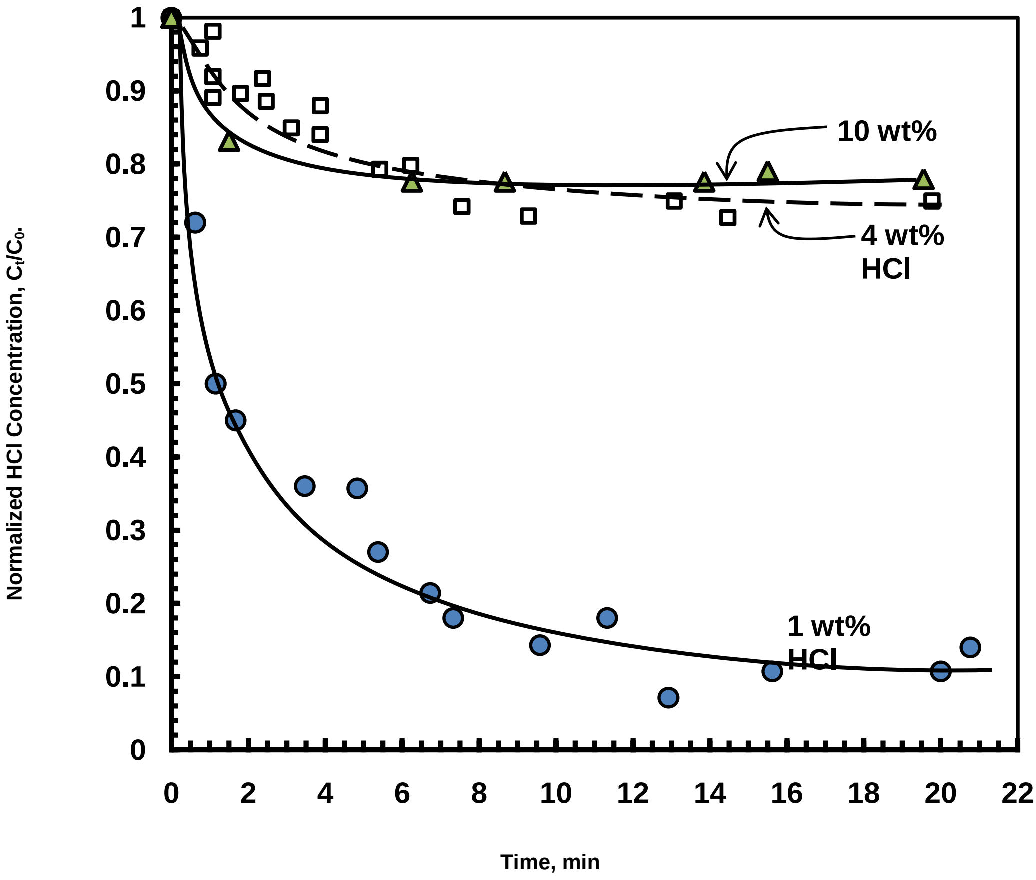


Fig. 9—Normalized concentration at various initial HCl concentrations, 190°F

TABLE 6—pH OF HCl SOLUTIONS BEFORE/AFTER HCl/Mn_3O_4 REACTIONS, 190°F

HCl Concentration, wt%	pH change in acid[7]	Decrease in pH value of DI water[8]	Gas release[9]
1	0.6 to 3.0	1 units	No countable bubbles observed
4	0.15 to 0.8	1 units	
10	0 to 1.0	3 units	A lot bubbles observed

---

[7] Change in pH of HCl acid solutions due to the reaction with Mn_3O_4 particles.

[8] Decrease in pH value of DI water due to release of chlorine gas and volatility of HCl. Experimentally, we observed decrease of 1 unit due to only the volatility of 10 wt% HCl at 190°F.

[9] Refer to chapter II.

Using visual cell experiment, GC/MS outputs showed that produced chlorine gas from HCl/Mn_3O_4 reactions depend on temperature and HCl Concentration (**Fig. 10**). The results indicated no chlorine gas detected from HCl/Mn_3O_4 reaction at 5 wt% HCl and 212°F for 24 hours soaking time. However, we identified chlorine gas when Mn_3O_4 particles were reacted with 5- or 15-wt% HCl at 284°F. We observed a much larger peak of chlorine gas at 15-wt% HCl than at 5-wt% HCl at the same temperature (Fig. 10). The presence of chlorine gas is a major concern because it is a toxic, corrosive, and a strong oxidizer.

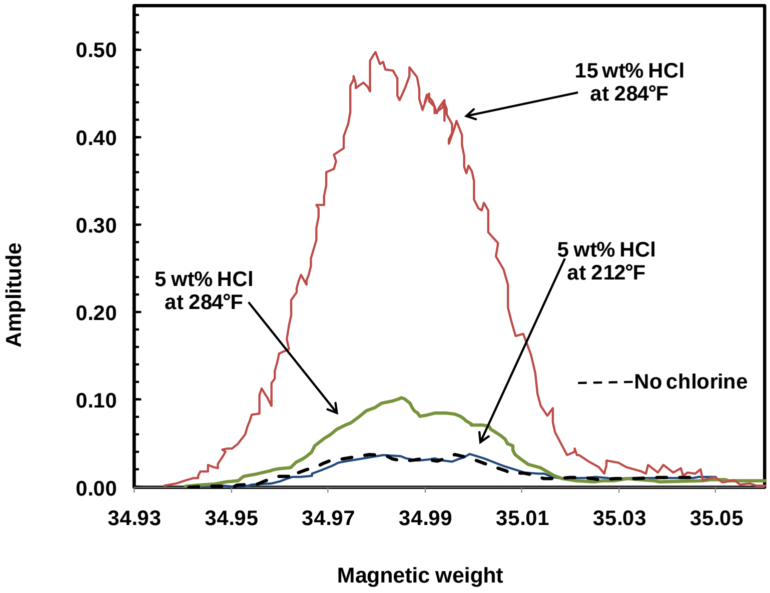


Fig. 10—GC/MS output shows chlorine gas produced during the reaction of Mn_3O_4 with 5 and15 wt% HCl at 284°F

From the available reactions in the literature, the best reaction that describes the obtained experimental results of 1- and 4-wt% HCl/Mn_3O_4 reactions at 190°F is:

$$Mn_3O_4 + 4HCl \rightleftharpoons 2MnCl_2 + MnO_2 + 2H_2O \quad \text{........................} \ (8)$$

Fig. 9 indicated about 0.9- and 1-wt% HCl consumed from HCl/Mn_3O_4 reactions at 1- and 4-wt% HCl, respectively. From Eq. 8 this should produce 6,700 and 7,400 mg/l soluble $MnCl_2$, respectively. Fig. 8 showed concentrations of manganese ions at 1- and 4-wt% HCl are about 7,500 and 8,500 mg/l, respectively. These results agree with Eq. 8 when taking into account the error due to sampling. XRD results indicated the solids remained after HCl/Mn_3O_4 reaction was mostly MnO_2 (**Fig. 11**). The color of MnO_2 was reported to be black as appeared in the obtained results (**Fig. 12**). In addition, according to Eq. 8, the weight of MnO_2 when 4 wt% HCl (200 grams) reacts with Mn_3O_4 (4 grams), should be 1.17 grams. Experimentally, the weight of remained solids (MnO_2) after the reaction was about 1.2 g which agrees with the theoretical value (Table 5). Assuming this is the correct reaction that describes the above equation, we conclude that chlorine gas was not produced in these experiments. Since HCl consumed almost completely (1-wt% HCl + 4 g Mn_3O_4), the reaction is irreversible as reported in the literature (Vadim et al. 2007).

Therefore, hydrochloric acid at 4-wt% is sufficient to dissolve most of Mn_3O_4 particles. HCl concentrations above 4 wt% HCl are not recommended to prevent chlorine gas release, especially at high temperatures.

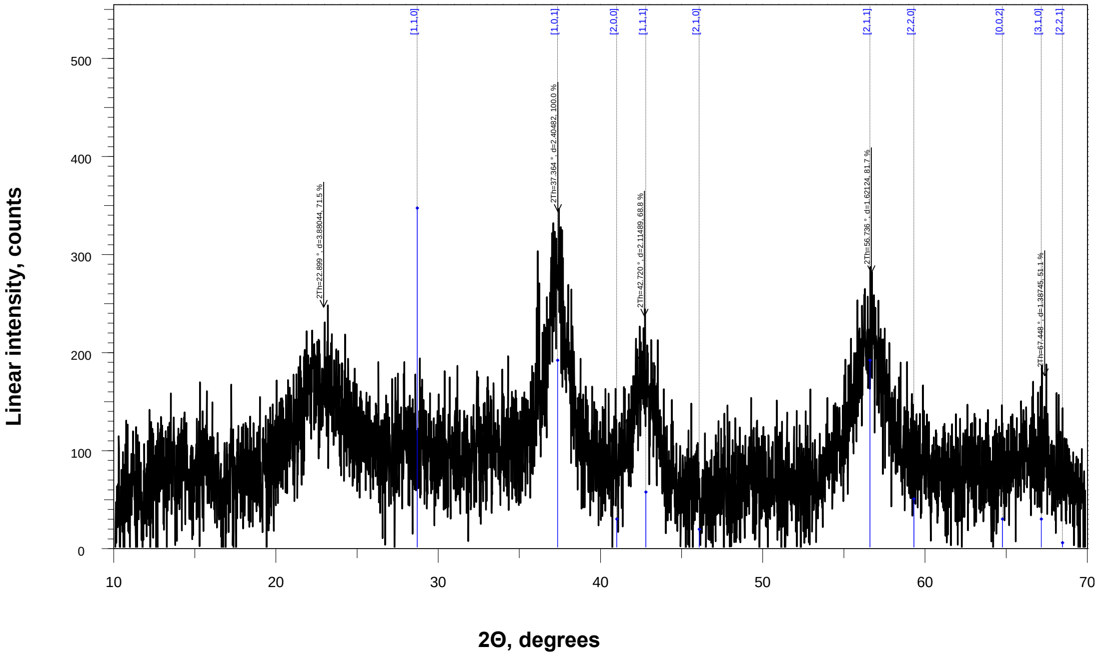


Fig. 11—XRD spectra of remained solids after the reaction of 4 wt% HCl with Mn_3O_4 particles showing the nature of the sample is nearly amorphous, with broad peaks corresponding mostly to MnO_2

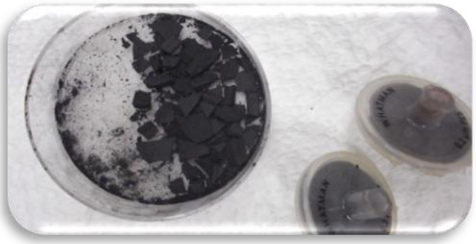


Fig. 12—Retained solids after the reaction of 4 wt% HCl with Mn_3O_4 at 190°F. The black solids of MnO_2 were noticed immediately after the reaction

Reaction of Organic Acids and Chelating Agents

Solubility of Mn_3O_4 Particles in Organic Acids and Chelating Agents

Solubility tests were first conducted on Mn_3O_4 particles as received. Five grams of Mn_3O_4 particles were soaked in 80-cm^3 of various cleaning solutions (**Table 7**) using visual cells w/o mixing of solutions. Sevendsen et al. (1995) suggested using citric acid to remove filter cake that is based on Mn_3O_4. Therefore, it was the first organic acid tested was critic acid. Tests were conducted using three citric acid solutions that contained 5-, 10- and 15-wt% citric acid at 77, 212, and 284°F.

TABLE 7—DESCRIPTION OF SELECTED CLEANING FLUIDS USED TO DISSOLVE Mn_3O_4

Chemical	Form	Density, g/cm^3	pH	Activity, wt%
precursor of formic acid	liquid	1.19	0.9	-
precursor of lactic acid	liquid	1.04	3.8	-
precursor of acetic acid	liquid	-	6.0	
acetic acid	liquid	1.05	-	99
formic acid	liquid	1.20	-	89
citric acid	solid	-	-	99
lactic acid	liquid	-	-	85
EDTA	solid	-	-	-
DTPA	liquid	1.13	12.6	-

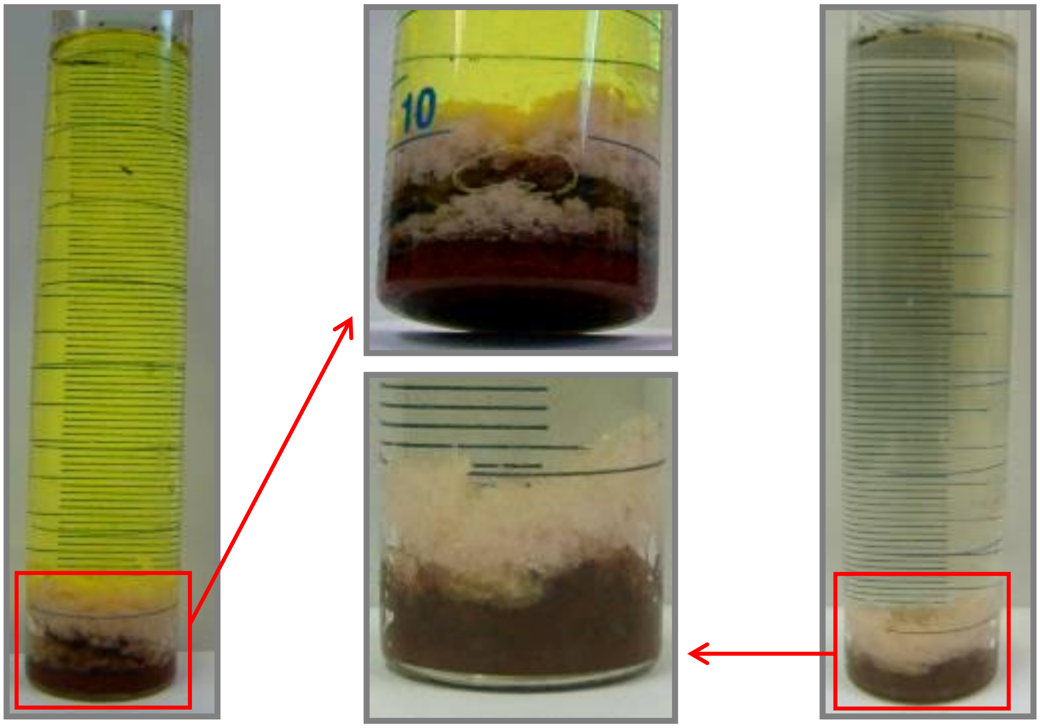
No precipitation was observed after 2 hours of reaction at 77°F. However, we noticed white precipitation after soaking times of 3-4 days (**Fig. 13**). Visual examination of the solids remained in the see-through cell after acid reaction revealed the presence of white crystals on the surface of Mn_3O_4 particles at temperatures of 212 and 284°F (**Figs. 14** and **15**). Because the precipitate formed on the surface of Mn_3O_4 particles, the solubility of Mn_3O_4 in citric acid (**Table 8**) determined by the solids weights before and after reaction with citric acid. **Table 9** gives the concentration of manganese in spent citric acid. Manganese concentration increased in solution as the initial concentration of citric acid was increased, especially at higher temperatures. Visual observations indicated that the amount of white precipitate increased with temperature and initial citric acid concentration.

5 wt% citric acid
Soaking time = 2 hours

10 wt% citric acid
Soaking time = 2 hours

10 wt% citric acid
Soaking time = 3-4 days

Fig. 13—Filtered solids from spent citric acid solutions with Mn_3O_4 particles at 77°F showed white precipitation after 4 days



212 °F

284 °F

Fig. 14—Spent citric acid solutions showed a white precipitate when 15-wt% citric acid reacted with Mn_3O_4 particles at 212 and 284°F after 24 hours soaking time

Fig. 15—Spent citric acid solutions with Mn_3O_4 showing the amount of formed white precipitation at 5 wt% acid less than at 10 wt% citric acid. The tests were at 284°F and 250 psi after 24 hours soaking time

TABLE 8—SOLUBILITY OF Mn_3O_4 AS A FUNCTION OF CLEANING FLUID TYPE, CONCENTRATION, AND TEMPERATURE. SOAKING TIME = 24 HOURS

Initial concentration,	Solubility, wt%		
	77°F	212°F	284°F
15 wt% formic acid	21.6	53.2	36.8
10 wt% formic acid	29.8	42	28.8
5 wt% formic acid	-	16.4	15.2
15 wt% citric acid	50.6	52.6	27.6
10 wt% citric acid	37.6	35.6	15.6
5 wt% citric acid	37	27.2	13.8
14.9 wt% lactic acid precursor (12 wt% acid)	-	51.6	-
11.7 wt% lactic acid precursor (9 wt% acid)	-	42.8	-
15 wt% formic acid precursor (9 wt% acid)	-	21.2	-
8.7 wt% formic acid precursor (5 wt% acid)	-	18.4	-
15 wt% acetic acid	6	10.2	-
10 wt% acetic acid	-	13.4	5.8
5 wt% acetic acid	-	7	10.1
20 wt% EDTA[10]	0	10	-
DTPA[11]-based chemical	2.4	6	7
15 wt% in-situ acetic acid (10 wt% acid)	-	3.2	-
10.2 wt% acetic acid precursor(7 wt% acid)	-	5.8	-

TABLE 9—MANGANESE CONCENTRATION IN SPENT ACIDS, SOAKING TIME = 24 HOURS

Initial concentration, wt%	Mn concentration in spent chemical, mg/l		
	77°F	212°F	284°F
15 wt% formic acid	17,819	12,970	17,351
10 wt% formic acid	9,556	22,333	9,646
5 wt% formic acid	-	5,453	4,622
11.7 wt% lactic acid precursor (9 wt% acid)	-	19,828	-
10.2 wt% acetic acid precursor (7 wt% acid)	-	6,358	-
15 wt% citric acid	4,521	5,693	5,816
10 wt% citric acid	2,681	3,955	5,881
5 wt% citric acid	3,680	2,736	3,848
15 wt% acetic acid	972	2,468	-
10 wt% acetic acid	-	4,043	-
5 wt% acetic acid	-	1,020	1,447
DTPA-based chemical	54	402	912
20 wt% EDTA	218	1	-

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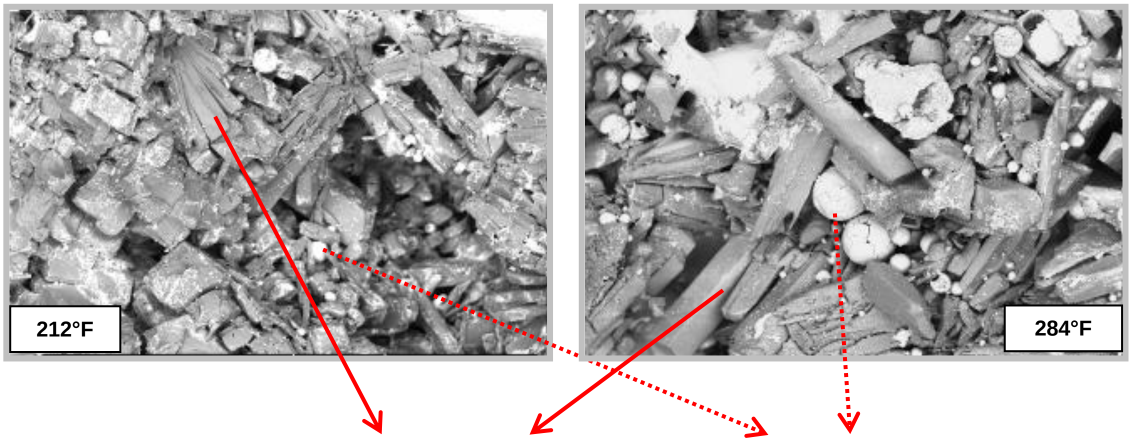
[10] Solids of NaEDTA

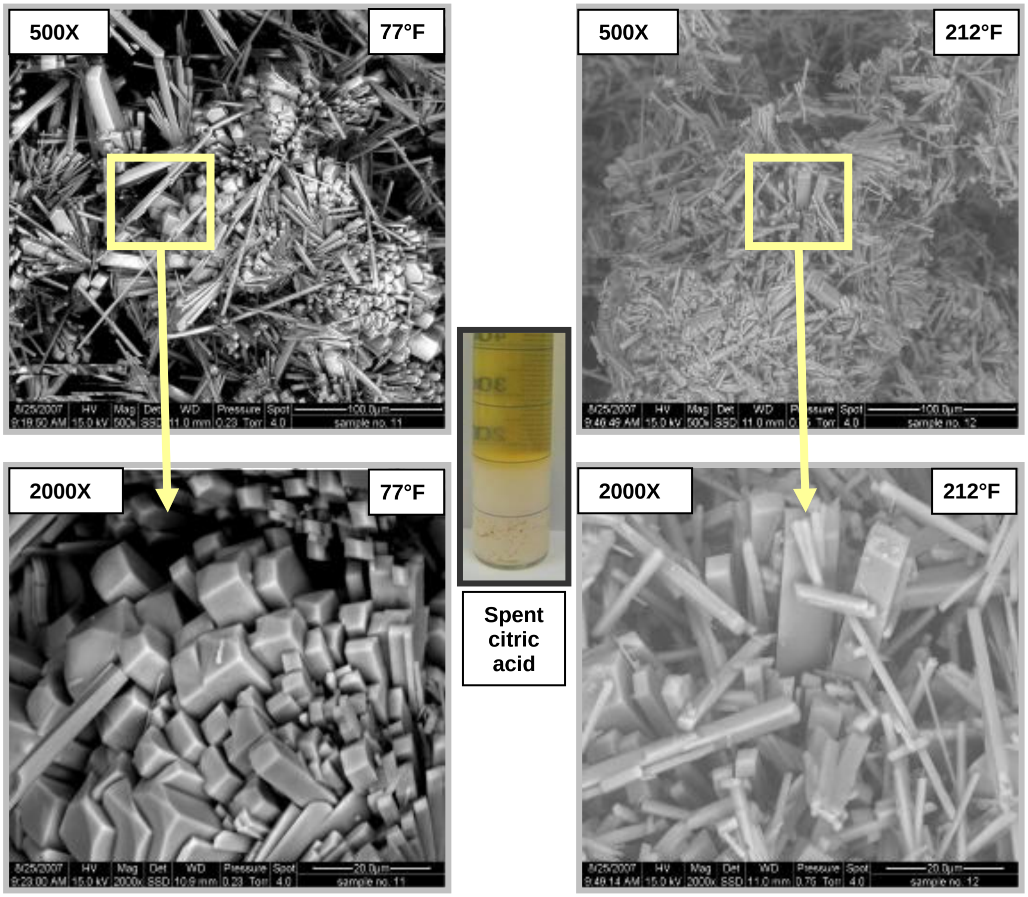
[11] Commercial chemical based on DTPA

Fig. 16 shows SEM photomicrograph of the solids filtered from the reaction of manganese tetraoxide with 15 wt% citric acid at 212 and 284°F. The samples had rectangular and spherical particles. The rectangular particles were white/light brown in color, whereas the spherical particles were brown. The rectangular particles contained manganese, carbon, and oxygen. Their concentrations were 22.3, 20.8, and 56.9 wt%, respectively. The concentrations of the three elements in manganese citrate, $Mn_3(C_6H_5O_7)_2.10H_2O$, are 22.8, 19.9, and 53.1 wt%, which agrees with the experimental values. The spherical particles contained 55.4, 3.4, and 41.2 wt% of manganese, carbon, and oxygen, respectively. The spherical particles most likely contained manganese citrate (small amount) and manganese oxides. A white precipitate was also found in the spent citric acid (**Fig. 17**) and the analysis of this precipitate indicated manganese citrate. The solubility of both lactic and citric acids were high, however, the reaction of lactic acid with Mn_3O_4 did not produce precipitation. This is because Mn(citrate) being linear chain polymer while Mn(lactate) are monomeric (Table 1) and citrate act as a bridge between manganese centers (**Fig. 18**)



Element	**Rectangular-shaped particles (light brown\white in color) wt%**	**Spherical-shaped particles (brown in color) wt%**
Mn	**22.3**	**55.4**
C	**20.8**	**3.4**
O	**56.9**	**41.2**

Fig. 16—Elemental analysis of filtered solids after 15 wt% citric acid/5 g Mn_3O_4 reaction at 212 and 248°F for 24 hours soaking time. BSE images show that the rectangular-shaped particles are rich in O and C (Mn citrate)



	Element, wt%		
	Mn	O	C
Average	32.1	49.3	18.7

	Element, wt%		
	Mn	O	C
Average	35.3	46.6	18.1

Fig. 17—ESEM analysis on white solids filtered from spent citric acid after the reaction with Mn_3O_4 at 15 wt% of the acid and temperatures of 77 and 212°F for 2 and 24 hours soaking time, respectively. The experiment was repeated three times

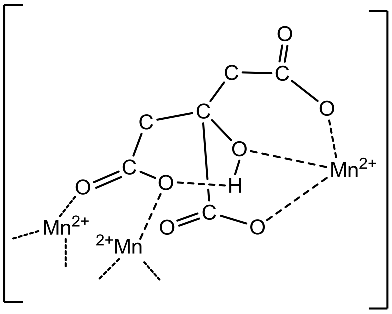


Fig. 18—Diagrammatic interpretation of manganese citrate shows citrates act as a bridge between manganese centers (Glusker and Carrell 1973)

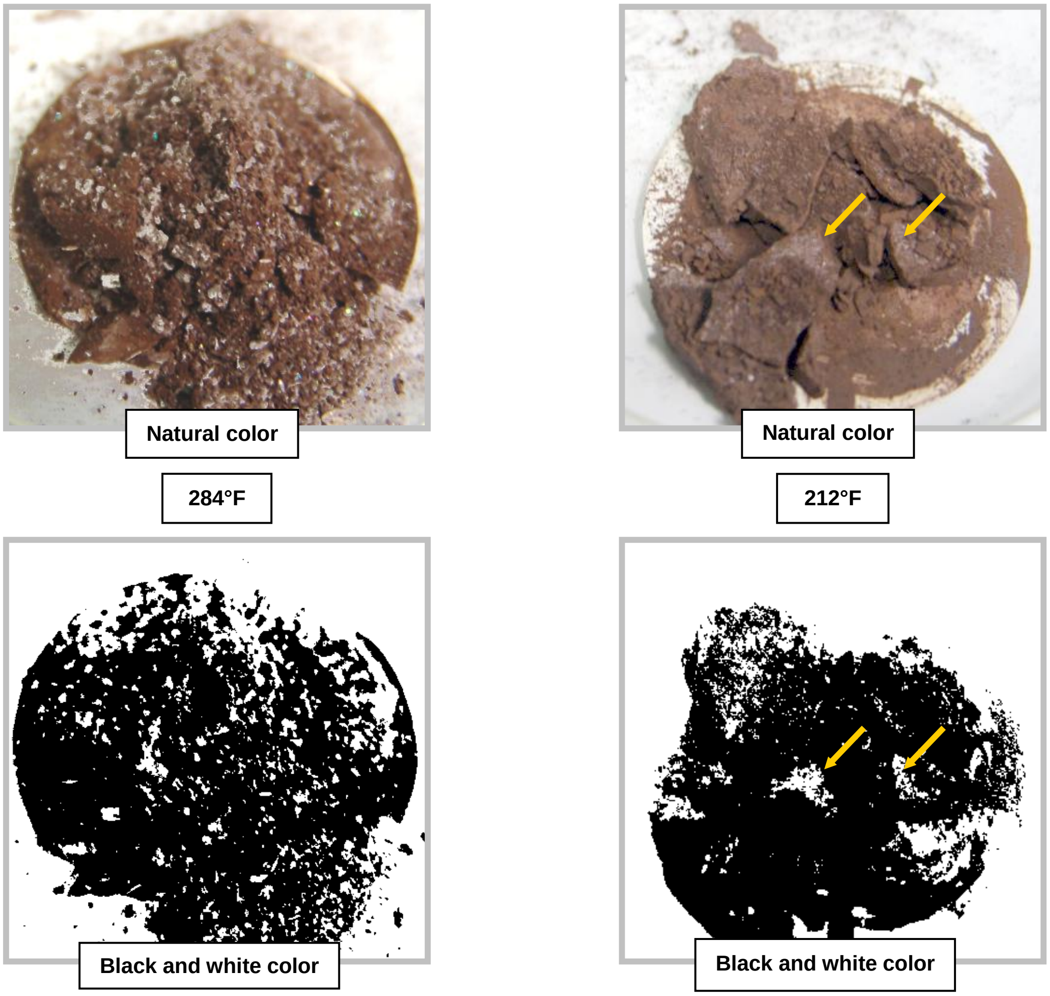
Other organic acids were also examined. Tables 8 and 9 give the solubility and the concentration of manganese in spent acids. A precursor of acetic acid (ester) or live acetic acid did not dissolve significant amounts of manganese tetraoxide particles. Formic acid and precursor of lactic acid (ester) dissolved more Mn_3O_4 than other tested acids. Their solubilities increased with acid concentration and temperature.

The gases produced from the reaction of the organic acids with manganese tetraoxide were bubbled in deionized water. The pH decreased from 6.5 to 4. Thus, it was decided to analyze the produced gases using gas chromatography. Nitrogen gas was used to pressurize the visual cell and displace air from the sampling cylinders. The results (**Table 10**) highlighted the presence of small, but significant amounts, of carbon dioxide and oxygen, which were produced from the reaction of organic acids with Mn_3O_4. It appears that Mn_3O_4 partially oxidize these organic acids.

TABLE 10—ANALYSIS OF GASES PRODUCED FROM Mn_3O_4/ORGANIC ACIDS REACTIONS

Gas	5 wt% lactic acid at 284°F	15 wt% lactic acid at 212°F	10 wt% acetic acid at 284°F	15 wt% acetic acid at 284°F
	mol%	mol%	mol%	mol%
Carbon dioxide	0.9	2.7	0.04	0.18
Oxygen	0.22	1.64	0.00	2.54
Nitrogen	98.87	95.66	99.96	97.28

Ethylene diamine tetraacetic acid (EDTA) at 20 wt% concentration and diethylene triamine pentaacetic acid (DTPA) did not dissolve significant amounts of Mn_3O_4 particles at pH about 12 (Tables 8 and 9). In addition, white and brown solids were noticed when DTPA was used at 212 and 284°F (**Fig. 19**).The amount of white solids (precipitate) increased with temperature. These solids were analyzed using SEM technique and the results are given in the tables shown in Fig. 19. Also, the silicon content in the precipitate increased with temperature. The presence of silicon at a high concentration in the white solids was interesting because Mn_3O_4 did not contain silicon (Table 2). The high pH solutions of DTPA dissolved some of the glass tube and released silicate in solution, which reacted with Mn and precipitated Mn silicates. The presence of this precipitate was a result of using a high pH DTPA solution in a glass graduated cylinder at high temperatures. However, similar reactions can occur during removing manganese tetraoxide from sandstone formations using high pH chelating agents. Precipitation of Mn silicates can cause formation damage, and extreme care should be taken when removing Mn_3O_4 using alkaline fluids in sandstone formations, especially at high temperatures. This is because manganese is very reactive when heated and thus it burns in nitrogen, oxygen, and chlorine and combines directly with Silicone (Greenwood and Earnshaw 1997). This explained the reaction with the silica in the glass graduated cylinder.



Element	White Solids wt%	Brown Solids wt%
Mn	2.7	55.6
C	2.1	1.6
O	52.1	38.6
Si	27.7	2
Fe	0.3	1.3

Element	White Solids wt%	Brown Solids wt%
Mn	29.6	62.9
C	1.4	0.8
O	39.8	31
Si	19.6	0.6
Fe	0.9	4.2

Fig. 19—Elemental analysis of filtered solids from DTPA/Mn_3O_4 reactions in glass graduated cylinders at 212 and 284°F, 250 psi using ESEM technique. The samples appear to contain white/light brown and brown solids

Solubility of Mn_3O_4-Based Filter Cake in Two-Stage Treatment

Several experiments were first performed to examine the efficiency of various cleaning fluids (**Table 11**) in removing filter cake. In a typical experiment, a filter cake was formed on a ceramic disk and one of the cleaning fluids was tested. A new filter cake was used to test each cleaning fluid. The filter cake was generated under dynamic conditions (100 RPM) where the cleaning fluids were soaked with filter cake at static conditions. The tests were conducted at 250 and 300°F and the pressure was kept at 250 psi. **Table 12** gives the number of cleaning stages, initial and final pH and acid concentration.

TABLE 11—FORMULA OF CLEANING FLUIDS USED TO REMOVE THE FILTER CAKE

Component	Precursor of lactic acid	Precursor of formic acid	Citric acid	Enzyme-A	Unit
Acid Precursor	10-15	15	-	-	wt%
Citric Acid	-	-	5-15	-	wt%
Enzyme-A[12]	-	-	-	10	wt%
Surfactant	0-0.2	0.2	-	-	vol%
Corrosion Inhibitor[13]	0.3-0.5	0.3	0.5	-	wt%
Formic Acid	-	-	-	-	wt%
pH Value at 77°F	3.7	2.1	0.9	4.7	-
Density at 77°F	1.044	1.065	1.052	1.031	g/cm^3

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[12] Enzyme-A is a starch specific enzyme (α-amylase)

[13] Corrosion inhibitors for formic and lactic acids were the same. A second corrosion inhibitor was used for citric acid.

TABLE 12—ACID CONCENTRATION AND pH OF VARIOUS FLUIDS BEFORE/AFTER CLEANING TESTS IN HP/HT FILTER PRESS

Cleaning fluid		Stages (No.)	Change in pH		Temperature		Soaking time		Acid concentration	Generated acid concentration
			pH_i[14]	pH_f[15]	°F		hours		C_f[16], wt%	CE[17], wt%
10 vol% lactic acid precursor		1 (M1)	3.7	3.0	250		15		4.95	8
15 vol% lactic acid precursor		1 (M3)	3.6	3.1	250		15		7.7	12
15 vol% lactic acid precursor		1 (M4)	3.7	3.3	250		46		5.85	12
15 vol% formic acid precursor		1 (M6)	2.1	1.9	300		46		4.6	8.7
10 wt% Enzyme-A	10 wt% LAP[18]	1(M15)	4.4	3.3	253		18		-	8
	5 wt% Citric acid	2(M19)	1.1	-	251	249	24	18	1.4	-
	5 wt% Citric acid	2(M21)	0.8	-	245	241	96	24	1.4	-
	12.5 wt% LAP	2(M22)	4.3	-	244	244	96	24	3.6	10
	5 wt% Citric acid	2(M24)	1	-	249	249	120	24	-	-

Table 13 give the filter cake solubility, soaking time, temperature and the ratio of initial and final brine flow rate. The procedure used in selecting the fluid and photos of filter cake before and after treatment with various cleaning fluids are shown in **Fig. 20**.

TABLE 13—CHARACTERISTICS OF Mn_3O_4-BASED FILTER CAKE BEFORE/AFTER CLEANING TESTS

No.	Cleaning Fluid		Stages	FC[19] solubility	Temperature.		Soaking Time		Brine discharge rates
					°F		hours		Efficiency,[20] %
M1	10 vol% lactic acid precursor		1	2	250		15		39.5%
M3	15 vol% lactic acid precursor		1	8	250		15		84.6%
M4	15 vol% lactic acid precursor		1	-	250		46		-
M6	15 vol% formic acid precursor		1	7.3	300		46		80%
M15	10 wt% Enzyme-A	10 wt% LAP	1		253		18		-
M19	10 wt% Enzyme-A	5 wt% Citric acid	2	31	251	249	24	18	-
M21	10 wt% Enzyme-A	5 wt% Citric acid	2	20	245	241	96	24	-
M22	10 wt% Enzyme-A	12.5 wt% LAP	2	84.1	244	244	96	24	93.6
A	10 wt% Enzyme-A	5 wt% Citric acid	2	54.4	249	249	120	24	44.7

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[14] **pH_i** = pH of acid solution before mud cake cleanup test.
[15] **pH_f** = pH of acid solution after mud cake cleanup test.
[16] **C_f** = Concentration of acid after mud cake cleanup test.
[17] **CE**, = Expected concentration of acid generated by the hydrolysis reaction of the ester at the test temperature and soaking time based on the results reported by Al Moajil et al. (2007).
[18] **LAP** = Lactic acid precursor (ester of lactic acid)
[19] **FC** = Filter cake
[20] **Efficiency** = (KCl brine flow rate in the last brine test) ÷ (flow rate in the 1st brine test) × 100

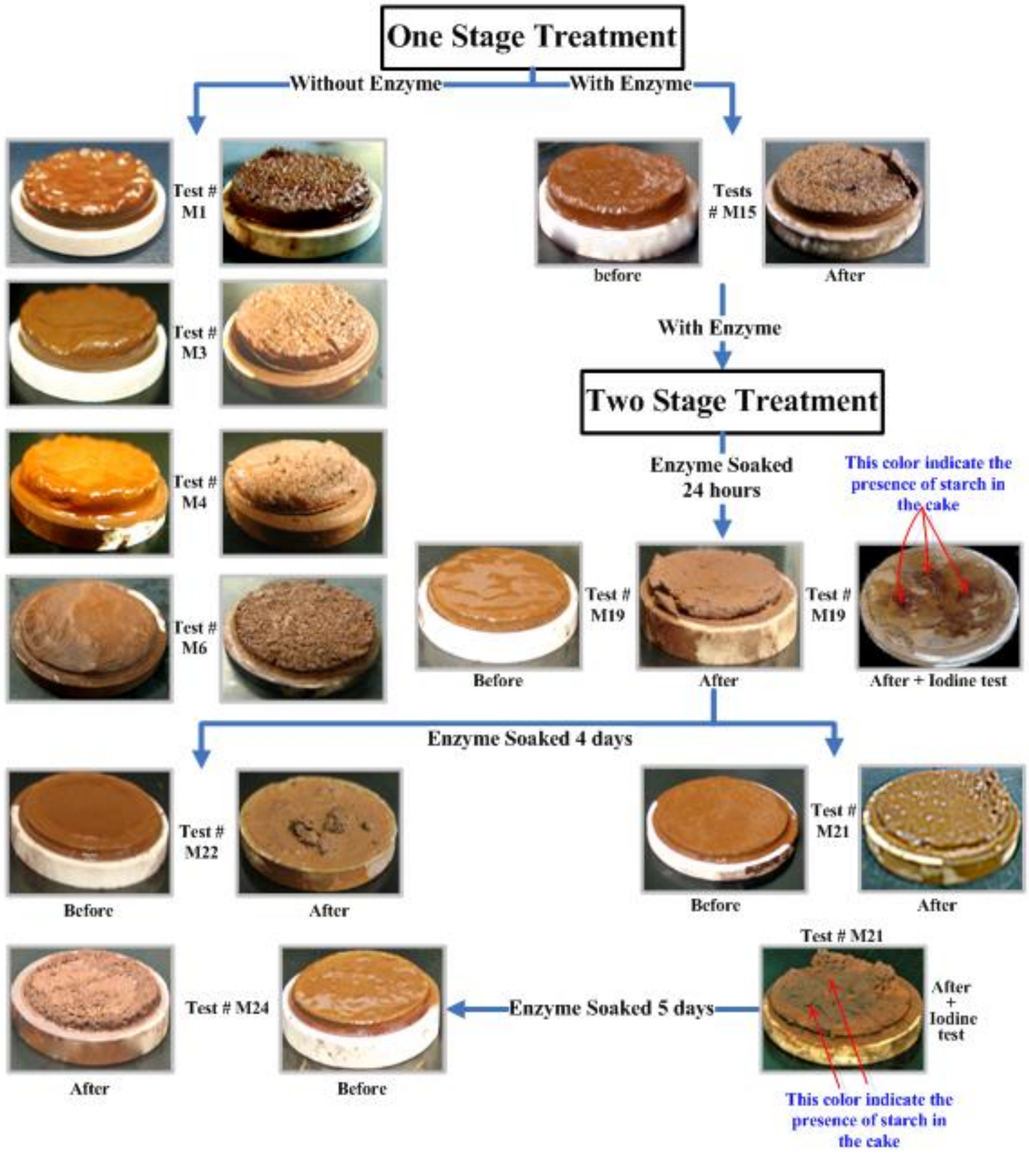

Fig. 20—Filter cakes before/after treatments showing a two-stage treatment is required to improve the solubility. P = 250 psi, T = 250-300°F, and soaking time = 15-46 hours

Precursors of formic and lactic acid at 10 and 15 vol% were used to remove the filter cake at different soaking times (Tables 12 and 13; Fig. 20). XRD/XRF results (**Tables 14** and **15**) indicate that these acids did not dissolve significant amounts of the filter cake. The cleaning fluids dissolved small amounts of calcium carbonate and manganese tetraoxide (**Table 16**). The highest manganese concentration was obtained when the filter cake was soaked in formic acid, for 46 hours at 300°F.

TABLE 14—CONCENTRATIONS OF MAIN ELEMENTS IN THE FILTER CAKE BEFORE/AFTER CLEANING USING EDXRF[21]

Element	Filter Cake before Cleaning		Filter Cake after Cleaning		
	Exp.M7, wt%	Exp. M1, wt%	Exp. M3, wt%	Exp. M4, wt%	Exp. M6, wt%
Mn	63.5	66.8	67.5	64	65
Fe	2.7	1.7	1.7	1.7	1.5
K	3.3	1.8	1.4	1.2	2.3
Ca	0.8	1.3	1.4	0.9	1.3
Cl	2.9	1.5	1.6	1.5	1.9
Si	0.1	0.1	0.1	0.1	0.1
Al	0.09	0.08	0.08	0.08	0.08

TABLE 15—MINERALOGY OF FILTER CAKE BEFORE/AFTER CLEANING TESTS USING X-RAY DIFFRACTION TECHNIQUE

Mineral	Filter Cake before Cleaning	Filter Cake after Cleaning			
	Exp.M7	Exp. M1	Exp. M3	Exp. M4	Exp. M6
Mn_3O_4	88	87	87	89	86
$CaCO_3$	4	7	8	5	7
KCl	8	6	5	6	7

TABLE 16—CONCENTRATIONS OF MAIN IONS IN THE CLEANING FLUIDS AFTER REACTION WITH THE FILTER CAKE

	Ion Concentration, mg/l			
Ion	Exp. M1	Exp. M3	Exp. M4	Exp. M6
Mn	6,547	13,322	15,194	22,006
Ca	792	560	663	919
Mg	35	43	53	3,726
K	35,795	31,193	44,057	42,788
Na	15,215	14,572	7,651	722
Total Fe	245	286	757	-

To explain the low solubility results obtained with organic acids, it was decided to examine the filter cake after soaking in precursor of formic acid, Mn_3O_4 particles, and the filter cake before containing the acid, using scanning electron microscope (SEM). There were large numbers of small particles after acid contact (**Fig. 21**). The small particles were attached to large ones, most likely by the polymers used in the drilling fluids. The polymer that hinders the reaction of organic acids with Mn_3O_4 particles is most likely starch. This is because the drilling fluid contain large

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[21] **M1-M6** = see Table 13

amount of starch in addition to its uses as a capping agent in the synthesis of Mn_3O_4 particles (Mu et al. 2006). Comparing **Figs. 21** and **22b**, it appeared that the size of the small particle decreased and their numbers increased after acid contact. A few calcium carbonate particles (cubical particles) disappeared after contacting formic acid. Obviously, the polymeric material that coated the Mn_3O_4 particles hindered acid reaction with the particles and, as a result, the cleaning efficiency of organic acids was very low. SEM results (**Fig. 23** and **Fig. 24**) of treated Mn_3O_4-based filter cake with lactic and formic acids showed two sizes, large (1-3 µm) and small (<0.1 µm).

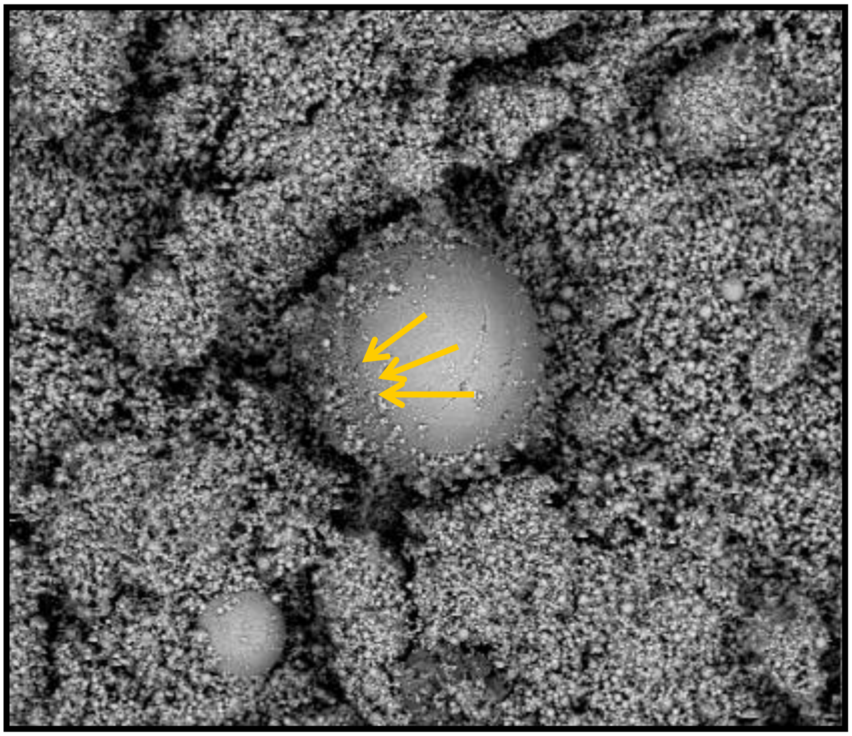
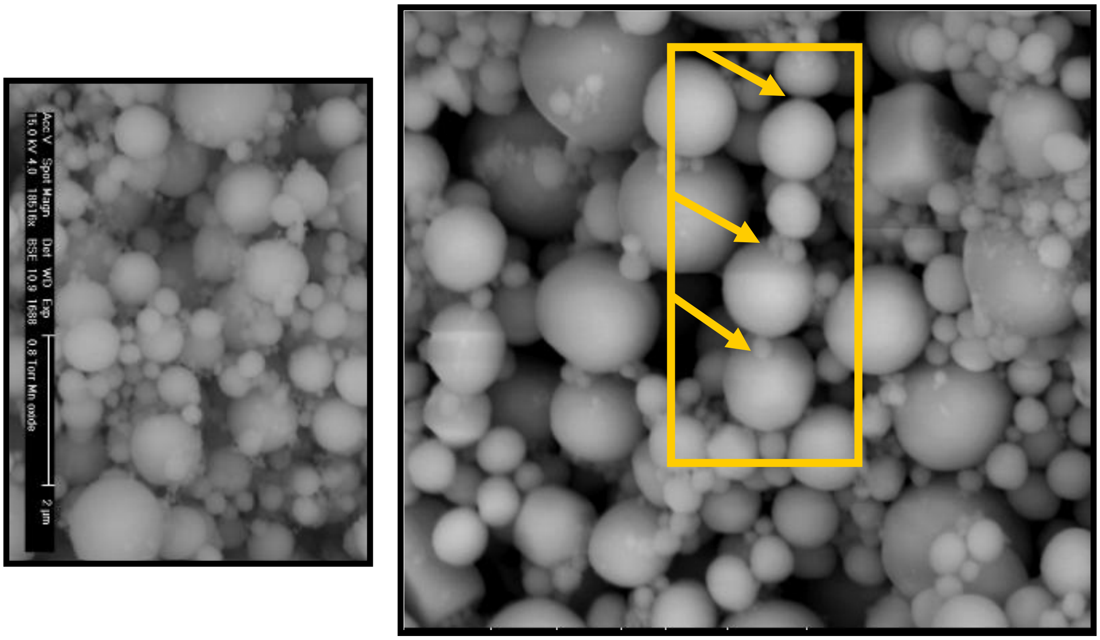


Fig. 21—SEM analysis of Mn_3O_4-based filter cake after soaking in 15 vol% precursor of formic acid for 46 hours at 300°F and 250 psi. The small particles appeared to be glued on larger particles, possibly by starch present in the filter cake. Magnification: 20,000X



a) Mn_3O_4 particles, 18,516X magnification

b) Untreated filter cake, 40,000X magnifications.

Fig. 22—a) BSE image of scattered Mn_3O_4 particles. b) BSE Image of untreated Mn_3O_4-based filter cake showing agglomeration of large and small Mn_3O_4 particles. The particles appear to be lined by a thin film of polymer (arrows)

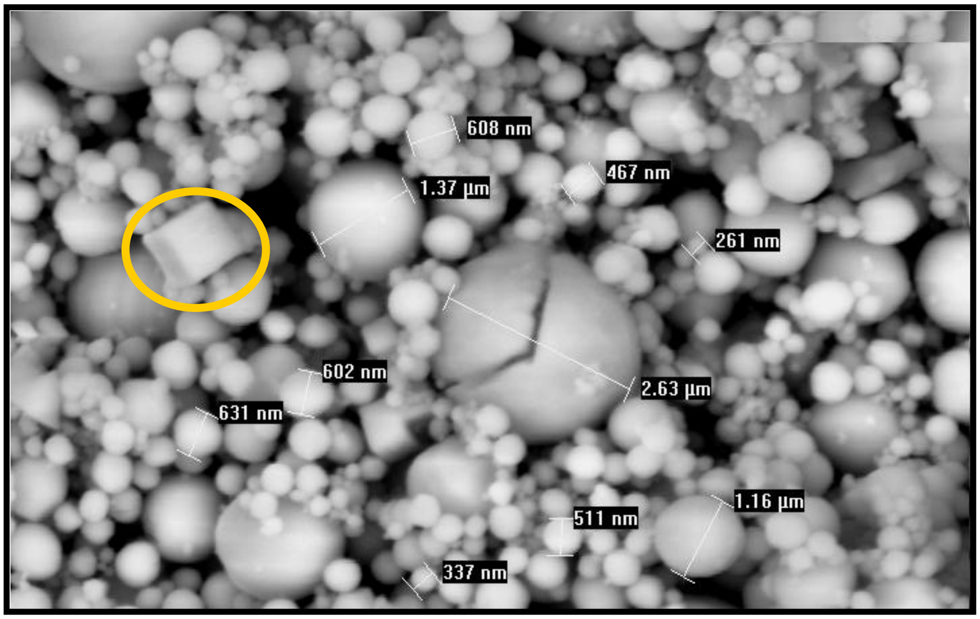


Fig. 23—SEM analysis of Mn_3O_4-based filter cake after soaking in 15 vol% precursor of lactic acid for 15 hours at 250°F and 250 psi. BSE image shows Mn_3O_4 particles in two sizes; large (1-3µm) and small (< 0.1 µm). Magnification: 9624X

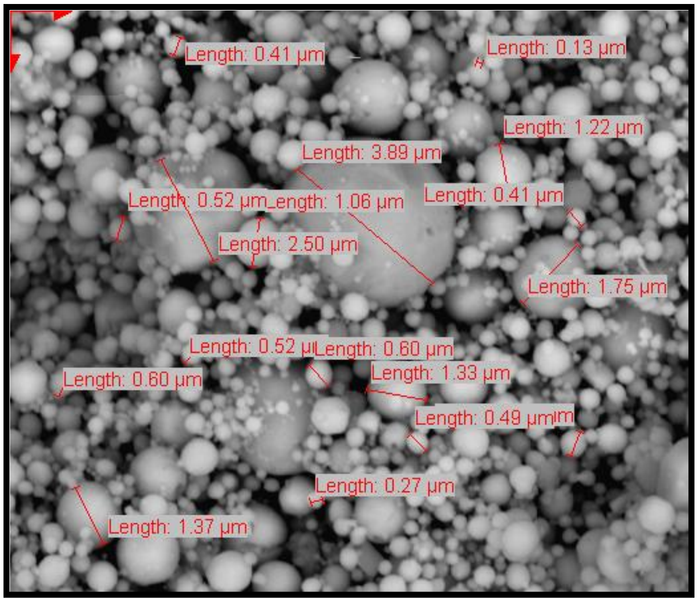


Fig. 24—SEM analysis of Mn_3O_4-based filter cake after soaking in 15 vol% precursor of formic acid for 46 hours at 300°F and 250 psi. BSE image shows size distribution of Mn_3O_4 particles. Magnification: 20,000X

To enhance acid-particles contact, there was a need to remove the polymeric material that coated the Mn_3O_4 particles. It was decided to start the cleaning process with a starch-specific enzyme, followed by an acid cleaning stage. Prior to using the enzyme treatment, it was essential to confirm the effectiveness of the enzyme to degrade starch. Thus, two solutions were prepared in two test tubes: the first tube contained starch and the second one contained starch and the enzyme. A few drops of an iodine solution were added to the solutions after incubating both tubes at 100°C for 24 hours. A blue color was noted in the first tube that contained starch, whereas no color was observed in the second tube, which confirmed that the starch was degraded by the enzyme (**Fig. 25**).

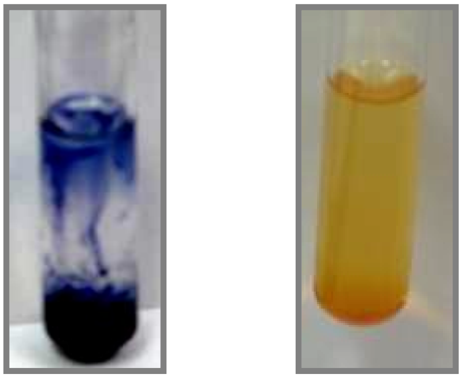


Fig. 25—Degradation of starch by enzyme-A can be followed using iodine test. The test tube to the left contains 2-wt% starch and the other tube contains in addition 2-wt% enzyme-A

Mixing the enzyme with an organic acid in a single-stage treatment precipitated. Compatibility tests were conducted to examine the possibility of mixing the enzyme with organic acids. Solutions that contained 10-wt% enzyme-A and 5-wt% of lactic, citric, or formic acid were heated in the visual cell at different temperatures. The enzyme was not compatible with these acids (**Fig. 26**), where the enzyme separated out of solution. To overcome this problem, a precursor of lactic acid was tested. At 77°F the precursor of lactic acid was compatible with the enzyme. However, when the temperature was increased, the precursor produced lactic acid, the pH of the solution decreased and the enzyme separated out of solution. These results indicated that this enzyme cannot be mixed with formic, lactic acids or their precursors, especially at high temperatures. This is because the enzyme is only compatible at specific pH ranges (pH>4).

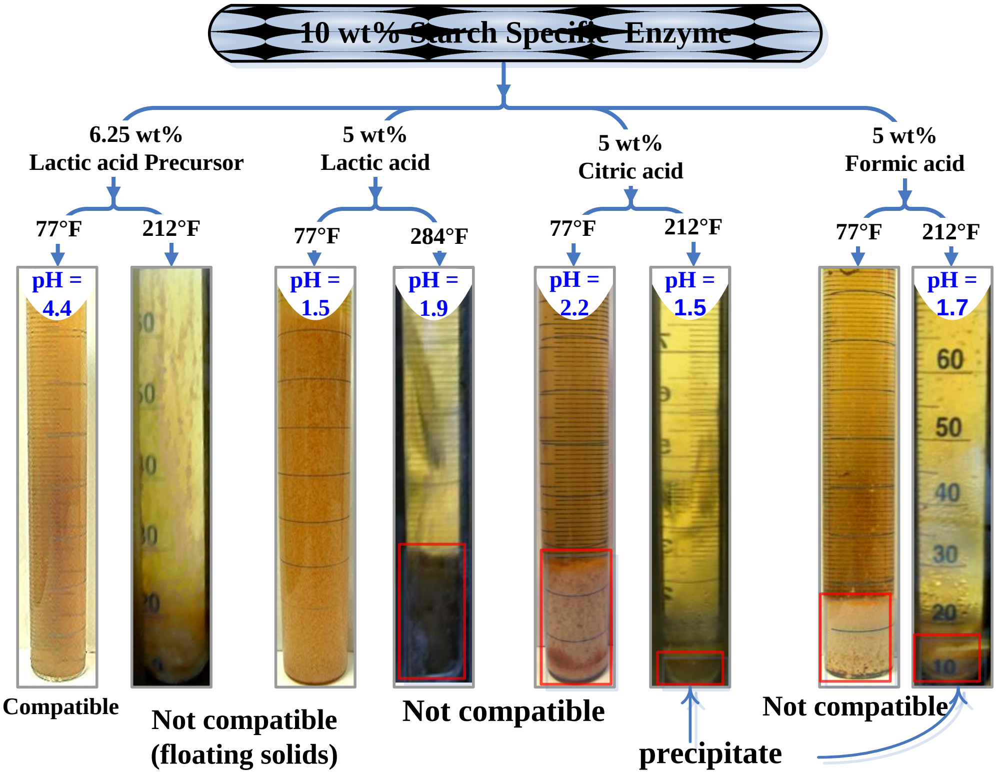


Fig. 26—Compatibility of organic acids with enzyme-A at different temperatures. The pH values were measured before conducting the tests

Based on the compatibility results, it was decided to remove the filter cake in a two-stage treatment. The objective of the first stage was to degrade the polymeric material that was present in the filter cake using enzyme-A, and then the second stage was used to remove manganese tetraoxide and calcium carbonate particles using a suitable acid system. It is found that the controlling step in dissolving the filter cake depended on the enzyme cleaning stage. A soaking time of 24 hours using 10 wt% enzyme-A with the filter cake was not adequate to remove the filter cake even after treating the mud cake with the acid (Fig. 20). The iodine test indicated that starch was still present in the samples after the enzyme treatment. Increasing the soaking time to 4 days did help in dissolving the filter cake in one test (test # M22); however in a second test (# M21) starch was noticed in the filter cake (Fig. 20). In test # M24, the enzyme soaking time was increased to 5 days and, as a result, the removal efficiency by the difference in filter cakes weights improved from 20 to 54%. The acid used in these experiments (M21 and M24) was 5-wt% citric acid and the reaction temperature was 250°F at 250 psi overbalance pressure. The acid soaked with filter cake for 24 hours. The removal of filter cake by citric acid was expected to improve by increasing acid concentration. However, a white precipitate produced from the reaction of Mn_3O_4 with citric acid was noticed in the experiments conducted with Mn_3O_4 particles. Therefore, it was decided not to increase the acid concentration. On the other hand, a precursor of lactic at 12.5 wt% (equivalent to 10 wt% lactic acid) (test # M22) was used after the enzyme cleaning step at the same conditions. The solubility of the filter cake was 85 wt% (Table 12 and Table 13 and Fig. 20).

Dissolving the filter cake created by Mn_3O_4 water-based drilling fluids using a two-stage treatment will increase the cost and time of the treatment (up to 5 days) which will result in delay of production operations. Increasing enzyme concentration will resolve the latter problem, although this will add more cost to the overall treatment. A cost-effective method is to combine a safe and small concentration of HCl with an organic acid in one stage treatment which found very effective as will be discussed in the following sections.

Solubility of Mn_3O_4 Filter Cake Using Acids Combination

To carefully understand the reactions of organic acids and chelating agents with Mn_3O_4 particles, we studied first the reaction kinetics of these chemicals, including acids investigated earlier. This also added more recommended organic acids to dissolve Mn_3O_4-based filter cake. We conducted the reactions with manganese tetraoxide particles at a temperature of 190°F and the weight ratio of acid/chelating agent to Mn_3O_4 was 50:1 (4 g Mn_3O_4/200 g acid solution). During each experiment, we collected and analyzed samples at different times as described earlier (Fig. 3). We tested a chelating agent (GLDA) and various organic acids, including organic acids investigated earlier.

Results indicated low to high solubility of Mn_3O_4 particles in the tested chemicals. Others produced precipitations upon the reaction with Mn_3O_4. The reaction time until equilibrium or completion reached varied from 5 to 100 mins. Additionally, acid gases were produced as results of the reaction with Mn_3O_4 (CO_2) with some of the acids. This is because the pH of deionized water decreased by 2 units (**Table 17**) when produced gases bubbled into the DI water as explained earlier in previous sections.

TABLE 17—pH OF ORGANIC ACIDS AND CHELATING AGENTS SOLUTIONS (200 g) BEFORE/AFTER THE REACTION WITH Mn_3O_4 (4 g), 190°F

Acid type (concentration, wt%)	pH change in acid[22]	pH change in DI water[23]	Spent acid density, g/cm^3
Oxalic acid (4)	**-**	**7 to 4.8**	**-**
H4-GLDA (19.9)	**1.8 to 2.2**	**7.1 to 5.3**	**1.290**
H3-GLDA (10.8)	**3.1 to 5.3**	**6.2 to 4.6**	**1.055**
D-Gluconic acid (4)	**2.2 to 3.9**	**6.1 to 5**	**1.019**
Lactic acid (4)	**2.2 to 4.0**	**6.1 to 5.2**	**1.018**
4 wt% Lactic acid + 1 wt% HCl	**0.6 to 3.1**	**5.6 to 5.1**	**1.025**
Malonic acid (2)	**1.7 to 3.6**	**No change**	**-**
Glycolic acid (4)	**1.9 to 3.6**	**No change**	**1.015**
Formic acid (4)	**2.0 to 3.3**	**No Change**	**1.022**
Butyric acid (4)	**2.6 to 3.9**	**No change**	**0.999**
Tartaric acid (4)	**1.8 to 3.0**	**No Change**	**-**
Propionic acid (4)	**2.5 to 3.4**	**No change**	**1.001**

D-Gluconic, Propionic, and Butyric, and acids were not recommended to dissolve Mn_3O_4-based filter cake. The results indicated low solubility values (**Table 18**) and Manganese concentrations in the spent acids were in the range from 450 to 3,700 mg/l (**Fig. 27**). The reaction time until equilibrium reached varied from 10 to 15 min (**Fig. 28**). Propionic acid has similar chemical structure to lactic acid (Fig. 4) except there is one hydroxyl group in the second carbon atom of lactic acid which makes it α-hydroxy acid. This hydroxyl group gives the acid a chelating ability. Therefore, the solubility of Mn_3O_4 particles in propionic acid is much lower than lactic acid as will be shown in the following paragraphs. On the other hand, D-gluconic acid is a multi-hydroxy acid (5 hydroxyl groups) but manganese concentration in spent acid is much lower than lactic acid. The reaction of Mn_3O_4 with D-gluconic or lactic acids depends on the chelate ring size. Larger ring size resulted in lower concentration of manganese ions in spent acids.

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[22] Change in pH of acid solutions due to the reaction with Mn_3O_4 particles

[23] Decrease in pH value of a DI water due to release of acid gases and/or acid volatility.

TABLE 18—SOLUBILITY OF Mn_3O_4 PARTICLES (4 g) IN ORGANIC ACIDS AND A CHELATING AGENT SOLUTIONS (200 g), 190°F

Acid type (concentration, wt%)	Dissolved solids, wt%	Manganese Concentration, mg/l	% of Consumed acid
4 wt% lactic acid + 1 wt% HCl[24]	99	14,600 at 10 min	66.5
Formic (4)	76.4	11,000 at 70 min	52.6
Glycolic (4)	74.5	10,000 at 30 min	66.5
Lactic acid (4)	70.2	8,900 at 35 min	75.9
Malonic (2)	53.73	6,600 at 25 min	60
d-Gluconic (4)	-	3,700 at 50 min	58.8
Butyric (4)	26.4	450 at 60 min	19.5
Propionic acid (4)	20.3	450 at 30 min	11.3
H3-GLDA (10.8)	-54.6 ppt[25]	12,200 at 76 min	35.2
Oxalic Acid (4)	-65.5 ppt	1,200 at 200 min	76.6
H4-GLDA (19.9)	-85.5 ppt	7,400 at 65 min	24.6
Tartaric (4)	-90 ppt	1,700 at 50 min	80

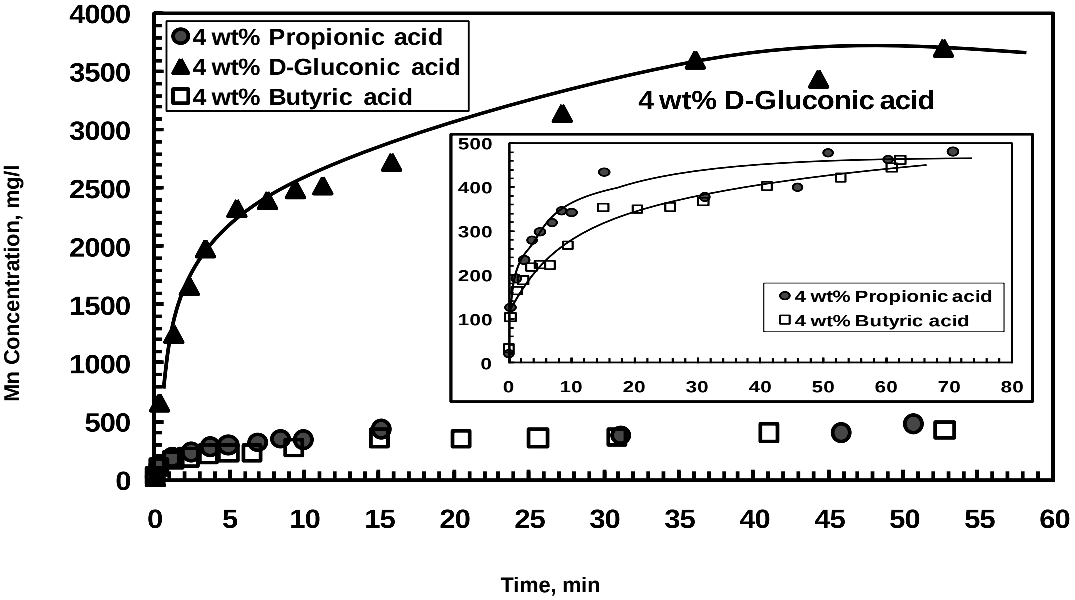

Fig. 27—Effect Mn_3O_4-low soluble organic acids on the dissolution of manganese ions, 190°F

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[24] If we assumed all HCl consumed as we explained in the text, then the final lactic acid concentration was 1.94 wt%.

[25] Ppt = precipitation. For example, (-54.6) mean the weight of solids increased by 54.6 wt%.

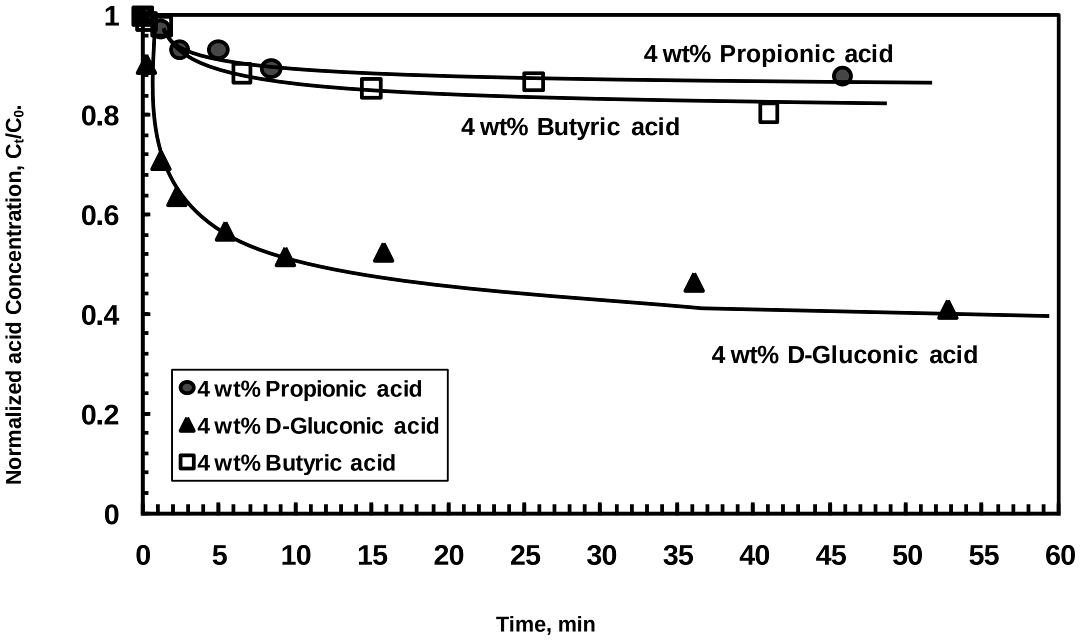

Fig. 28—Normalized acid concentration of Mn_3O_4-low soluble organic acids, 190°F

Therefore, Selection of acid with proper structure is essential to effectively treat Mn_3O_4-based filter cake. Because of the low solubilities of EDTA, DTPA, acetic, propionic, butyric, and gluconic acids, they will not dissolve enough amount of Mn_3O_4-based filter cake.

We noticed earlier in this study low solubilities of Mn_3O_4 particles in either EDTA or DTPA at high pH (~12). A recent study suggested treating Mn_3O_4 at lower pH ranges (Peña et al. 2007). Therefore, two chelating agents derived from glutamic acid were tested (H3-GLDA and H4-GLDA). They refer to amino polycarboxylic acids class of chelating agents such as EDTA. H4-GLDA (pH=1.7) has four carboxylic groups and one nitrogen atom (Fig. 5). When a hydrogen atom in one carboxylic group is replaced by sodium atom, GLDA is referred to as H3-GLDA (pH=3). Manganese ions concentration in spent GLDA after the reaction with Mn_3O_4 reached completion was higher with H4-GLDA than H3-GLDA (**Fig. 29**). However, these reactions produce high amount white precipitation (Tables 17 and 18).

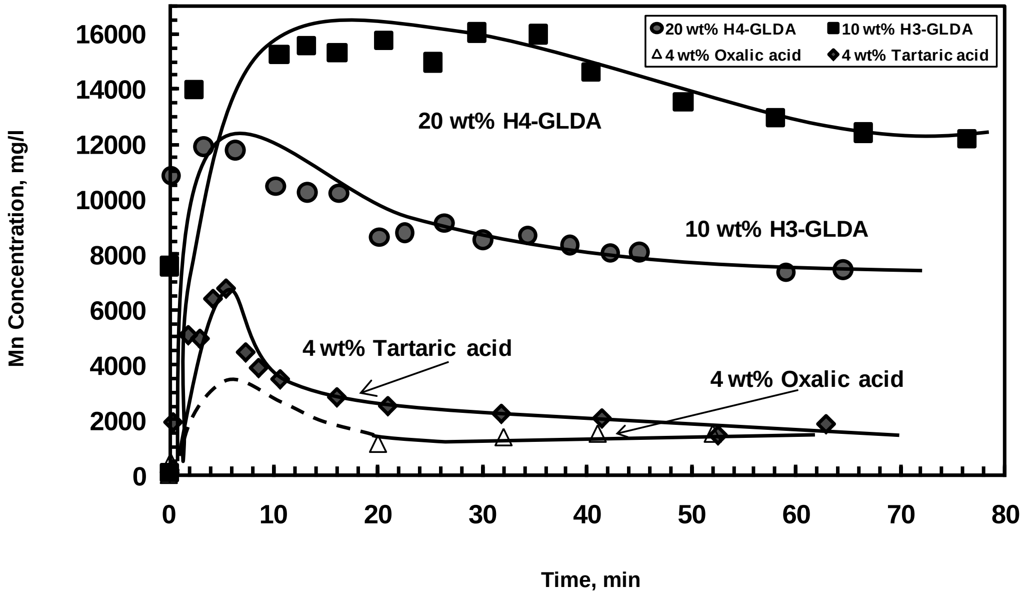

Fig. 29—Effect Mn_3O_4-precipitate producing organic acids on the dissolution of manganese ions, 190°F

Gases produced from the reactions were bubbled through deionized water. The pH of the DI water decreased by ~2 units (Table 17) which indicated release of acid gas (e.g. CO_2). The decrease in GLDA concentration indicated acid/base reaction rather than only chelation reaction (**Fig. 30**). Similar observations noticed with oxalic and tartaric acids except that there was no indication of produced gases with tartaric acid (Tables 17 and 18; Figs. 29 and 30).

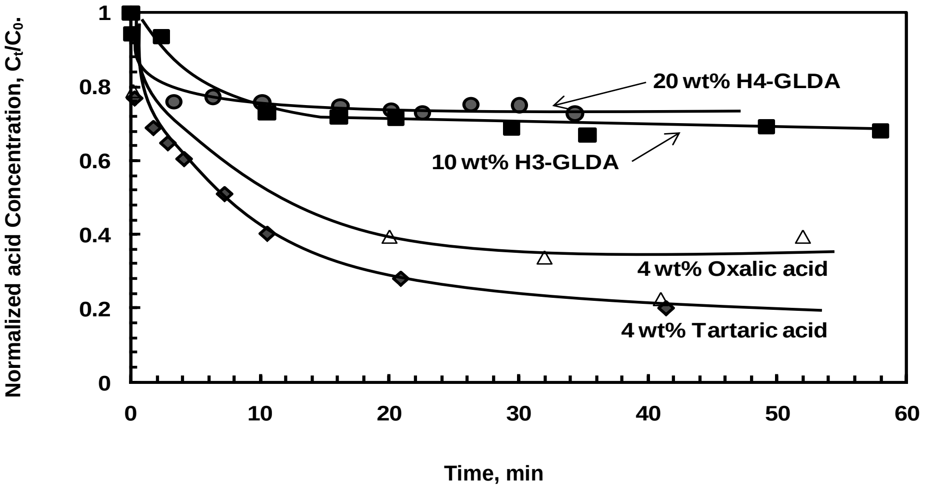

Fig. 30—Normalized acid concentration of Mn_3O_4-precipitate producing organic acids, 190°F

Therefore, Mn_3O_4 oxidized GDLA and produced damaging material. This is because of the catalytic properties of Mn_3O_4 and most probably the presence of amine group in GLDA (Fig. 5). Because of Mn_3O_4 active phase, it can catalyze the NO/NH_3 reduction reaction as discussed in the first chapter which explained the obtained results from GLDA/Mn_3O_4 reactions. Oxalic acid (Fig. 4) produced insoluble white products. The explanation is analogous to citric acid reactions (Fig. 18), explained earlier. Tartaric acid (i.e. diacid) chemical structure is a combination of two lactic acids. However, it produced white precipitate different from lactic acid reactions. Therefore, GLDA, DTPA, oxalic, tartaric, and citric acids are damaging chemicals. The reaction of these chemicals with Mn_3O_4-based filter cake will result in formation damage. EDTA is a damaging only in sandstone formation as explained earlier.

The remaining acids dissolved significant amount of Mn_3O_4 particles and solubilities up to 76 wt% achieved at 190°F (Table 18). These are formic acid, two α-hydroxy acids (lactic and glycolic), and a diacid (malonic acid). Lactic, glycolic, and formic acids at 4-wt% dissolved 70, 75, and 76 wt% of Mn_3O_4 particles, respectively. Malonic acid at lower concentration (2 wt%) dissolved 54 wt% of Mn_3O_4 particles. The highest manganese ions concentrations at equilibrium achieved with 4 wt% formic acid (11,000 mg/l). Manganese ions concentrations in spent lactic and glycolic acids were 9,000 and 10,000 mg/l, respectively. The reaction rate of formic acid was the slowest among the other organic acids (**Fig. 31**).

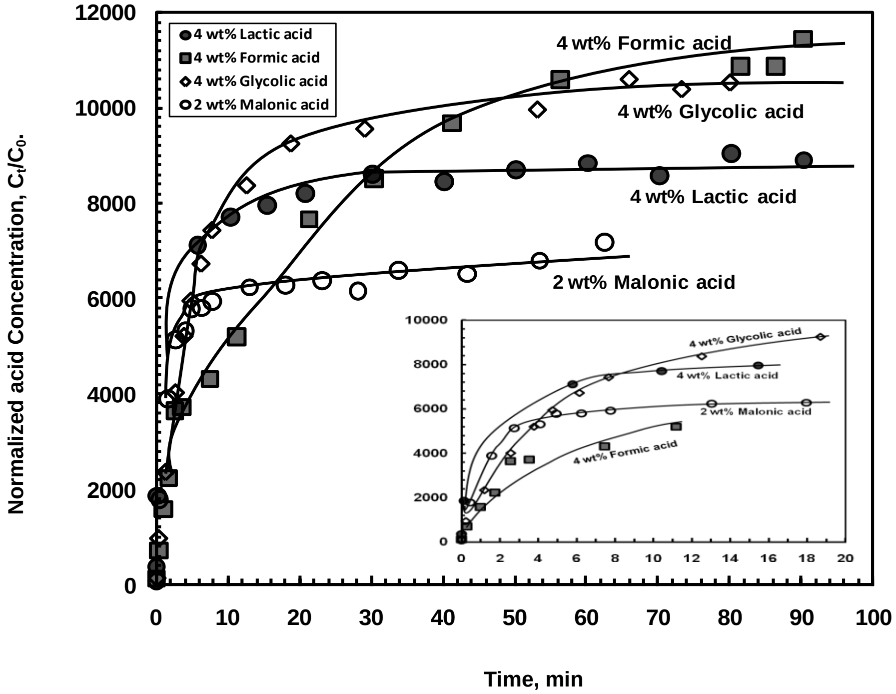

Fig. 31—Effect Mn_3O_4-high soluble organic acids on the dissolution of manganese ions, 190°F

No clear observations of produced gases with formic, lactic, glycolic, and malonic acids at 190°F (Table 17). Earlier discussed experiments showed that Mn_3O_4/lactic acid reaction produced carbon dioxide and oxygen at 212 and 284°F (Table 10).

Organic acids exhibit much lower corrosion rates than HCl. However, there is always acid left after filter cake removal treatments during flowback of spent acid. Selection of acid that mostly spent during these treatments would further reduce the corrosion effects in the flowback of spent acid. Among the above recommended acids, lactic showed the highest spent acid, 77 wt% of lactic acid consumed (**Fig. 32**).

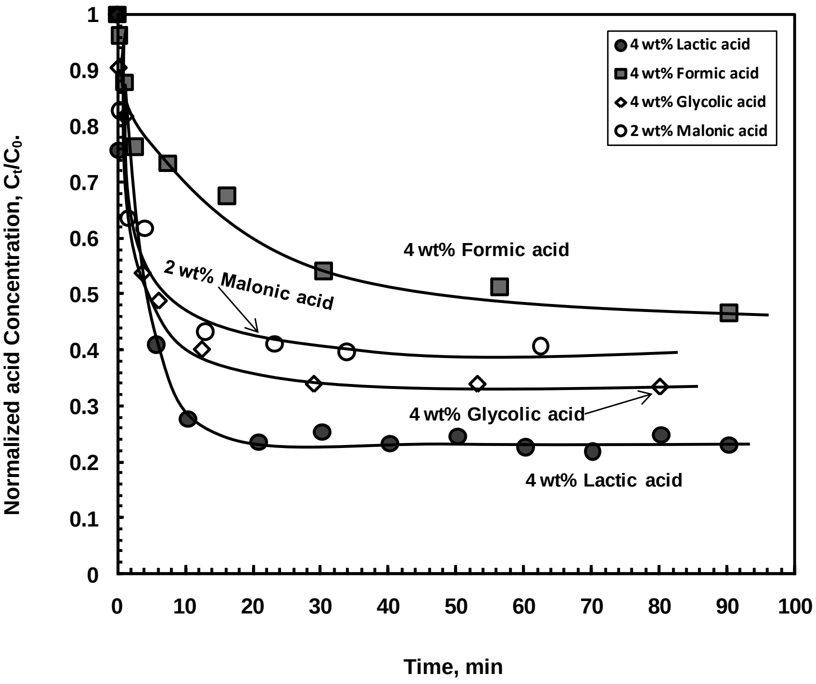

Fig. 32—Normalized acid concentration of Mn_3O_4-high soluble organic acids, 190°F

Combining low and save concentration of HCl with a Mn_3O_4-high soluble organic acid lead to an innovative approach to dissolve Mn_3O_4-based filter cake and Mn_3O_4 particles in one-stage treatment. We selected lactic acid because it is available as a commercial cleaning fluid, have further chelation ability, and the most consumed acid among the high soluble organic acids. The obtained results can be generalized to formic, glycolic, and probably malonic acids. Complete solubility of Mn_3O_4 particles achieved when1-wt% HCl combined with 4-wt% lactic acid (Table 18). HCl or lactic acids alone (4-wt%) dissolved only about 70 wt% of Mn_3O_4 particles at 190°F (Tables 5 and 18). **Fig. 33** showed almost complete dissolution of manganese ions when HCl and lactic acids are combined (~15,000 mg/l) while the dissolution was lower when either of the acids was used alone. Complete dissolution of manganese ions was calculated as 18,000 mg/l, which agrees with the experimental value when taking into account the error because of sampling. The results further showed much higher reaction rate than using lactic acid alone and 68 % of combined HCl/lactic acids consumed (**Fig. 34**). HCl consumed completely as the pH of spent acid increased to 3.1 and the remaining was about 2-wt% lactic acid.

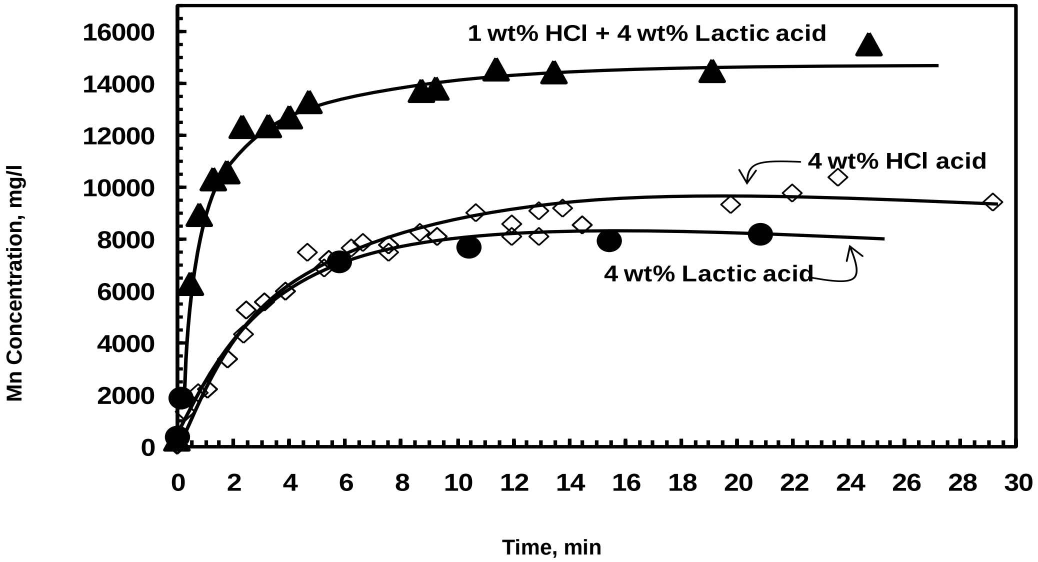

Fig. 33—Dissolution of manganese ions showing higher Mn concentration with HCl/lactic acid combination than only lactic acid alone, 190°F

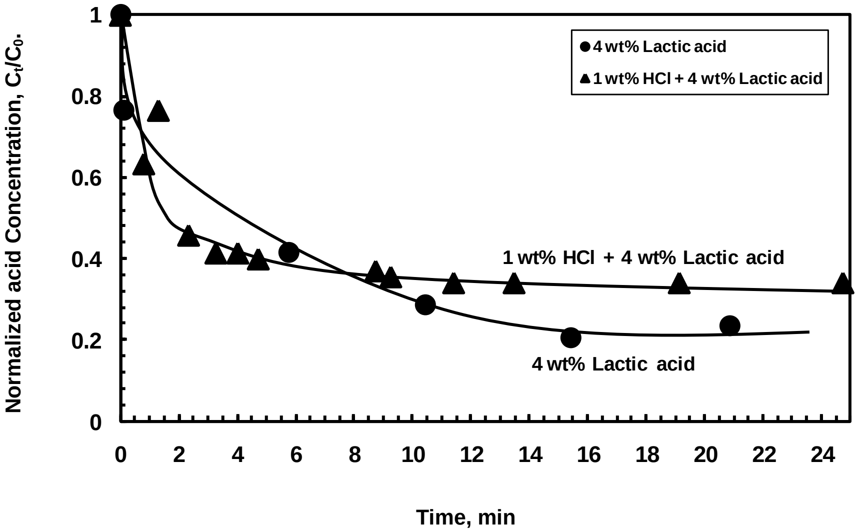

Fig. 34—Normalized acid concentration of HCl/lactic acid combination and lactic acid, 190°

HCl/lactic acid solution (300 g), at 1-wt% HCl and 4-wt% lactic acid, dissolved 85 wt% of Mn_3O_4-based filter cake after 18-22 hours soaking time at 250°F and 250 psi (**Figs. 35** and **36**). After 9 hours of the reaction with the filter cake the pH of the HCl/lactic acid spent solution increased to 3.4 which indicate the complete consumption of HCl (Fig. 35). The filter cake solubility was 45 wt%. The acids solution were mixed with the filter cake during the soaking period where the previous discussed filter cake removal experiments were done at static conditions. Combining HCl with formic, glycolic, and probably malonic will lead to similar results. Previous discussed outcomes are either consists of two-stage treatment (enzyme and organic acid) with higher acid concentration and longer soaking times (up to 5 days) or high HCl concentration that resulted in similar filter cake solubilities. Thus, the combined HCl/organic acid approach showed great advantages over previous discussed methods.

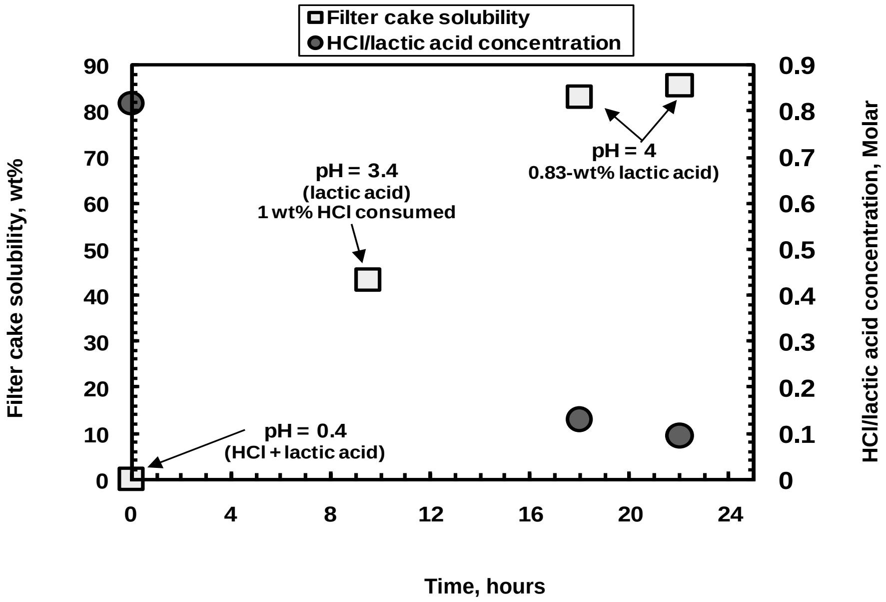

Fig. 35—Solubility of Mn_3O_4-based filter cake and acid concentration using 1-wt% HCl/4-wt% lactic acid at 250°F and 250 psi. The acids solution was mixed during dissolving the filter cake

Before Cake thickness = 0.174	**After 9.5 hours** Cake thickness = 0.157	**After 18 hours** Cake thickness = 0.026	**After 22 hours** Cake thickness = 0.024

Fig. 36—Mn_3O_4-based filter cakes before/after the reaction of (1 wt% HCl + 4 wt% lactic acid) at 250°F and 250 psi

CHAPTER IV

CONCLUSIONS

We developed three effective solutions to dissolve the filter cake created by water-based drilling fluids weighted with manganese tetraoxide particles. Hydrochloric acid alone can hydrolyze polymeric content and dissolve Mn_3O_4 particles in the filter cake. Dissolving the filter cake in two-stage treatment of enzyme and organic acid was found to be effective and eliminated the associated drawbacks of using HCl (mainly the production of chlorine gas at high HCl concentrations). However, this will lead to a longer and more costly treatment. Considering these disadvantages, we found that combining low and save concentration of HCl (<5 wt%) with an effective organic acid in one-stage treatment was very effective.

We arrived to these solutions after the extensive study on both the reaction of Mn_3O_4 particles alone and the filter cake solubility with several cleaning fluids at different reaction temperatures and soaking times. Those include HCl, simple organic acids, hydroxy acids, diacids, and amino carboxylic acids (chelating agents). Based on the results we classified them into Mn_3O_4-low soluble, -high soluble and -damaging acids.

The cleaning fluids selection was mainly based on the recommendations in the petroleum industry to dissolve the filter cake created by various drilling fluids and other literatures that studied the reactions of Mn_3O_4 particles with several chemicals. The following sections summarize the main conclusions and recommendations based on the obtained results.

Summary

(1) Hydrochloric acid (10 wt%) dissolved 78 wt% of Mn_3O_4-based filter cake at 250°F and 28 hours soaking time in a one-stage treatment.

(2) At temperature of 190°F, 1- and 4-wt% HCl dissolved most Mn_3O_4 particles (56- to 70-wt% solubility), while the solubility was complete at 10 wt% HCl. Generally, the solubility increased with HCl concentration and temperature up to 284°F.

(3) Chlorine gas was detected during the reaction of 5- to 15-wt% HCl with Mn_3O_4 particles especially at high temperatures (up to 284°F).

(4) The reaction of 1- and 4-wt% HCl with Mn_3O_4 particles was found to follow Eq. 8 at 190°F introduced by De (1975) which further confirmed the absence of chlorine gas production at HCl concentrations lower than 5-wt%.

(5) We found the reaction time needed until completion reached at 10-wt% HCl is less than half that of 1- and 4-wt% HCl with Mn_3O_4 particles at 190°F. Generally, the reaction time is fast and within a few minutes.

(6) The results on EDTA and DTPA at high pH (12) and acetic, propionic, butyric, and gluconic acids at low pH (3-5) showed very low solubilities of Mn_3O_4 particles.

(7) A white precipitate of manganese citrate was noticed following the reaction of citric acid with Mn_3O_4 up to temperatures of 284°F. The amount of precipitation increased with temperature and initial acid concentration.

(8) GLDA reacted with Mn_3O_4 particles completely at 190°F.However, a large amount of white precipitation produced. Similarly, a white precipitation was observed with oxalic and tartaric acids.

(9) The reaction of DTPA with Mn_3O_4 particles in glass cylinder produced Mn(silicate) at 212 and 284°F.

(10) At acid concentration of 4-wt%, lactic, glycolic, and formic acids dissolved significant amount of Mn_3O_4 particles and solubilities up to 76 wt% achieved at 190°F. Malonic acid at lower concentration (2 wt%) dissolved 54 wt% of Mn_3O_4 particles at the same temperature.

(11) Small but significant amounts of carbon dioxide and oxygen were produced from the reactions of Mn_3O_4 with lactic and acetic acids at 212 and 284°F. It appears that Mn_3O_4 oxidized the acids partially and produced these gases. This can be generalized to other organic acids.

(12) Manganese tetraoxide particles were covered with polymeric material, which significantly reduced the solubility of filter cake in organic acids. Therefore, it was very important to remove this material before addressing the removal of Mn_3O_4 using organic acids.

(13) Starch specific enzyme was not compatible with formic and lactic acids and this can be generalized to low pH acids (pH<4).

(14) A two-stage treatment of enzyme and organic acid was found to be effective in removing Mn_3O_4-based filter cake. 12.5-wt% precursor of lactic acid (≈10 wt% generated lactic acid) and 10-wt% enzyme dissolved 84 wt% of the filter cake. The enzyme stage was the controlling step which requires up to 5 days soaking time. Increasing the enzyme concentration is expected to reduce the soaking time. Glycolic, formic, and most probably malonic acids can be used in place of lactic acid in the acid stage.

(15) An innovative approach lead to complete solubility of Mn_3O_4 particles when low and safe concentration of HCl (1-wt%) combined with 4-wt% lactic acid at 190°F.

(16) HCl (1-wt%) combined with lactic acid (4-wt%), dissolved 85 wt% of the Mn_3O_4-based filter cake after 18-22 hours soaking time at 250°F in one stage treatment. Combining HCl with formic, glycolic, and most probably malonic acids would lead to similar results.

Recommendations

(1) HCl concentration above 5 wt% is not recommended to dissolve Mn_3O_4-based filter cake when the risks associated with corrosion and chlorine gas production cannot be handled especially at high temperatures (above 212°F).

(2) HCl concentration at 2- to 4- wt% is enough to dissolve most of Mn_3O_4-based filter cake and certainly cause disturbance to the filter cake (Fig. 35).

(3) Damaging chemicals including GLDA, citric, oxalic, and tartaric acids are not recommended to dissolve the filter cake created by Mn_3O_4 particles. In addition to the low solubility of DTPA with Mn_3O_4 at high pH, it will cause formation damage in sandstone formation specifically.

(4) Because of the low solubility of Mn_3O_4 with EDTA and DTPA at high pH (12) and acetic, propionic, butyric, and gluconic acids at low pH (3-5), they are not recommended to remove Mn_3O_4-based filter cake.

(5) Lactic, glycolic, formic, and malonic acids or their precursors are recommended to dissolve Mn_3O_4-based filter cake when only combined with low and save concentration of HCl (<5 wt%) or used in two-stage treatment of enzyme and the organic acid.

(6) Malonic acid above temperatures of 140°C is not recommended because it decarboxylate at temperatures from 140 to160°C.

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