IRON INDUCED SLUDGE TESTING FOR CO_2 FLOOD PILOT PROJECT

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Abstract

Sludging is an ever present problem in the Permian Basin. Recent studies have shown the influence of iron by-products on the sludging process. Questions have emerged concerning effects of CO_2 introduction into the overall reaction. An operator concerned with this over-all process began a study to determine the influence of CO_2 on the over-all system. The results of this study involving a San Andres CO_2 pilot program are evaluated. Included are compatibility testing of produced oil, produced water and acid systems. Testing was conducted with and without iron injected into the system. A representative cross-section of the field lease crude and produced water was utilized. Considerations for future CO_2 flood testing are discussed.

Background

Many studies have been conducted to evaluate the cause, effect and control of acid sludge in oil-bearing reservoirs.[1-9] The most general definition of an acid sludge is a deposition of asphaltic components contained in the crude oil. This deposition is the result of destabilization of the colloidal material in equilibrium with the other hydrocarbons in the reservoir crude prior to production. Destabilization as reported in the literature can be caused by changes in the reservoir fluid composition through normal production life of the well. Low pH or neutralization of basic components in the reservoir crude which maintain the stability is also proposed. The last cause is the presence of ferric (Fe^{+3}) ions in the acid treating fluids.[3,6] Some crude oils develop acid sludge just from the presence of an acid, while others are not affected until ferric ions are present. Permian Basin lease crudes tend to fall more in the latter category. This organic deposition is extremely detrimental to both production and injection. In addition the removal or cleanup is difficult and expensive.[2,3]

Iron is a source of many problems in the petroleum industry, elimination or reduction of iron in the fluids being pumped into reservoirs has a major effect on the success of any well work.[3-6] Typically, the sources of iron that pose these problems are the tubulars that are being pumped through (mill scales and rust), service company equipment used to transport and/or pump the fluids and to a lesser degree the downhole tools.[7] Several methods are practiced to mitigate or minimize the effects of iron. These include tubing cleanouts, where the tubulars are pretreated to remove as much of the soluble iron as possible before fluids are pumped into the reservoir. Another is the addition of chemicals in the fluids to control soluble iron through chelation or reduction. The reduction of Fe^{+3} to Fe^{+2} has been found to have the most significant effect on control of acid sludge development, resulting from soluble iron in acid solutions.

We have minimal control on the effects of reservoir fluid composition during normal production operations. However, there is one area of concern over which we have some control and that is the effect of CO_2. In CO_2 floods where breakthrough has occurred asphaltic sludge has been a concern.[1] Where acid stimulations are being pumped, acid sludging has been attributed to the CO_2 breakthrough interactions. A study of CO_2 effects on produced oil and water compatibility could provide an understanding of sludge development and whether CO_2 poses a potential problem. In addition, evaluation of acid systems designed to prevent acid sludge need to be evaluated for effectiveness in the presence of CO_2.

Procedure

Evaluations of acid and oil compatibility at ambient temperature and under atmospheric pressure conditions without CO_2 were performed on 27 San Andres wells located in a CO_2 pilot program. Each sample of oil and water tested was obtained no more than 24 hours prior. The acid system tested was 15% hydrochloric acid containing 5000 ppm total iron in a 3:1 ratio Fe^{+2}:Fe^{+3}. The additives included a corrosion inhibitor, reducing agent, reducing agent catalyst, surfactant and anti-sludge agent (**Table 1**). These tests were performed in accordance with API's RP-42[10] procedure for acid sludge testing.

The above tests were also duplicated using a modification to the above referenced acid sludge test to ascertain effectiveness in the presence of CO_2. The reservoir oil to be tested was filtered and placed in a water bath, controlled to a value equal to reservoir temperature (90°F). Simultaneously, the acid system to be tested was also placed in this bath. Both were conditioned in the bath for 10 minutes. A 100 mL sample of each fluid was blended together with an emulsifier blade at 10,000 to 15,000 rpm's for one minute. This mixture was rapidly placed into a Baroid 500 mL Corrosion Test Cell (**Figure 1**) and pressurized to 900 psi using CO_2. The pressurized chamber was then placed back in the water bath for 30 minutes. After this the chamber was inverted and pressure released. The chamber was opened and the contents poured into a graduated cylinder through a 100 mesh screen, which was checked for solids. Percent separation in the graduated cylinder was also observed and reported.

In addition to the acid sludge testing, complete water analyses of all produced water samples was performed. Compatibility of the produced oil and produced water in the presence of CO_2 were evaluated at 90°F. This compatibility test procedure was performed in like manner to the acid and oil compatibility testing with CO_2 with one exception- the blended sample was poured through a 400 mesh screen after 30 minutes of heating.

Test Results

The titrametric analyses of San Andres produced water (**Table 2**) have been reported in parts per million. Iron concentrations range from 0.1 ppm to 10.0 ppm. These low iron concentrations would not be considered high enough to be damaging to formation productivity under normal conditions. However, when CO_2 is introduced into the acid system, a more stable emulsion is formed (**Table 3**). Emulsion break times were recorded at specific intervals of 5, 10, 20 and 30 minutes. None of the lease crudes in **Table 3** were observed to have sludge formed when evaluated with the acid system. Columns in **Table 3** labeled

50:50 represent an equal volume of formation water blended with produced oil and tested with CO_2 added. In nearly every case, testing with CO_2 required a longer time period to separate or break. Where break times of 10 minutes or more were noted in the No CO_2 column, 95% of the emulsion was broken in five minutes. This was true for all but one case, number 347, which was 97% broken in 10 minutes. Emulsion break times of the 50:50 blends closely matched the acid system containing CO_2. However, a comparison of the tests of the 50:50 fluid blends to the tests with the acid system without CO_2, shows that not only are the emulsions more stable, but six of the lease crudes tested generated sludge.

Titrametric water analysis did not indicate sufficient iron to explain sludging so atomic absorption analysis were conducted on eight wells (**Table 4**). The analysis indicated a possible cause for the sludging, strontium. The fluid testing on well number 282 is of particular interest. Constituent analysis indicates only 0.5 ppm iron (0.2 by AA), an amount not generally considered sufficient to generate sludging and stabilize an emulsion. This lease crude when tested with the acid system, which broke other emulsions, formed a stable emulsion and sludge (**Table 5**). Concentrations of reducing agent were increased to 6 gpt and catalyst to 2 gpt to attempt to prevent the formation of sludge. It was successful in preventing sludge, but still required 30 minutes for the emulsion to break. The 50:50 blend of formation water and produced oil for this well also formed a stable emulsion and sludge. Atomic Absorption analysis indicated that this well had the highest concentration of strontium (**Table 4**) of all the produced waters tested. Data from well 313 produced water indicated a moderate amount of strontium (**Table 4**), but it also formed a stable emulsion and generated sludge with the 50:50 blend and CO_2 (**Table 3**). The lease crude tested with the acid system did break the emulsion in 30 minutes and did prevent sludging.

Conclusions

1. Acid system additives provide effective emulsion break and prevention of sludge from San Andres crudes in the presence of CO_2.

2. High levels of strontium appear to stabilize emulsions and induce the formation of sludge in blends of San Andres crude and produced water in the presence of CO_2.

3. Proposed reservoirs for CO_2 flooding should be studied for the potential of reservoir damage associated with sludge formation as the result of CO_2 interactions with the reservoir fluids.

4. An update is needed of standard testing procedures for evaluation of sludge formation and emulsion stability including the effects of metalic ions, CO_2, and other components of the reservoir.

References

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Table 1
Acid System 1 Additives

Additive Name	Description
1 gpt Corrosion Inhibitor	A blend of organic materials added to the acid to control corrosion of the tubulars at an acceptable level.
3 gpt Iron Reducing Agent	Organic material that with the aid of a catalyst provides reduction of Fe^{+3} to Fe^{+2}, even in live acid.
1 gpt Catalyst	Metallic source that catalyzes the reducing agent above.
4 gpt Surface Active Agent	Organic blend that provides control of emulsion stability to facilitate rapid separation of acid and reservoir oil.
4 gpt Anti-Sludge Agent	Organic material that aides in the dispersion of asphaltic particles, stabilizing them from coagulation.

Table 2
Titrametic Water Analysis

Number	SpGr	pH	R_w	Iron	Ca^{+2}	Mg^{+2}	SO_4^{-2}	HCO_3^-	Cl^-	Na^+ & K^+
359	1.058	6.37	0.10	0.1	2,117	804	2,225	1,326	47,259	28,208
372	1.057	6.37	0.11	6.0	2,422	828	2,105	1,397	47,682	28,115
334	1.033	6.34	0.17	0.1	1,936	776	3,388	1,335	27,880	16,516
342	1.038	6.50	0.12	0.4	2,042	632	3,444	1,034	25,819	15,244
339	1.038	6.48	0.16	10.0	2,312	726	2,325	846	26,975	14,860
330	1.038	7.02	0.14	0.8	1,927	819	2,408	1,281	30,443	17,619
347	1.040	6.62	0.13	1.5	2,308	794	1,875	1,079	33,846	19,105
353	1.067	6.29	0.09	1.0	2,699	683	2,275	1,040	50,234	29,604
319	1.023	6.76	0.15	1.0	1,955	570	1,417	954	17,595	9,128
313	1.043	6.60	0.12	0.1	2,301	699	2,000	1,263	37,967	22,056
341	1.038	6.50	0.12	0.4	2,042	632	3,444	1,034	25,819	15,244
312	1.033	6.81	0.16	1.0	2,285	635	1,975	1,488	30,591	17,493
343	1.050	6.78	0.17	1.0	2,248	764	3,452	1,027	33,143	19,549
318	1.035	6.67	0.22	1.0	1,932	1,033	1,449	919	32,850	18,175
346	1.070	6.52	0.08	6.0	2,168	772	1,893	992	53,084	31,760
360	1.040	6.48	0.16	2.0	2,115	701	3,125	1,032	31,154	18,337
329	1.043	6.50	0.12	1.0	1,419	536	2,517	1,018	32,598	20,089
282	1.035	6.80	0.00	0.5	7,729	5,823	4,831	1,155	34,396	5,170
340	1.035	6.63	0.14	0.5	2,396	775	3,623	990	28,599	16,440
320	1.038	6.51	0.16	0.1	2,197	773	1,700	1,246	31,985	18,016
317	1.028	7.14	0.20	0.1	1,829	638	1,556	1,448	22,568	12,622
333	1.030	6.70	0.20	3.0	1,825	849	3,398	1,362	23,301	13,551
374	1.078	6.10	0.08	4.0	2,672	902	2,087	1,030	55,659	32,715
354	1.035	6.74	0.16	3.0	2,010	751	2,250	1,155	28,986	16,548
369	1.051	6.91	0.12	8.0	3,349	971	1,736	929	42,626	23,147
370	1.032	6.52	0.18	10.0	1,938	659	2,422	1,336	30,620	18,051
358	1.023	6.74	0.30	0.3	1,329	546	1,906	1,181	19,550	11,478
357	1.043	7.14	0.15	2.0	2,071	862	2,157	983	32,215	18,289

Table 3
Emulsion and Sludge Test Results

	Emulsion Break Time			Sludge
	System 1		50:50	50:50
Number	No CO_2	w/CO_2	w/CO_2	w/CO_2
359	5	10	10	No
372	5	10	10	No
334	5	10	10	No
340	10	20	10	No
342	10	10	10	No
339	10	10	10	No
330	5	10	10	No
347	20	10	10	No
353	5	10	10	No
319	5	10	10	No
313	10	30	Stable	Yes
341	10	10	10	No
312	5	30	Stable	Yes
373	10	10	10	No
343	10	10	10	No
318	5	10	10	Yes
346	5	10	10	Yes
360	5	10	10	No
329	5	10	10	Yes
317	5	10	10	Yes
333	10	10	10	No
374	10	10	10	No
354	5	10	10	No
369	10	10	10	No
370	10	10	10	No
358	5	10	10	No
357	10	10	10	No

Table 4
Atomic Absorption Analysis

Number	Barium	Strontium	Iron	Manganese
346	0.4	73	0.5	0.25
333	0.5	40	1.2	0.67
339	0.2	93	0.2	0.09
282	1.1	112	0.2	0.11
340	0.4	79	0.1	0.18
320	0.7	44	0.1	0.2
319	0.5	36	0.1	0.3
313	0.4	57	0.2	0.29

Table 5
Emulsion and Sludge Tests Well 282

Acid System 1 w/CO_2		50:50 w/CO_2		Comments
Emulsion Break Time	Sludge	Emulsion Break Time	Sludge	
30	No	---	---	System 1 w/150 psi CO_2
30	Yes	---	---	System 1 w/900 psi CO_2
30	Yes	---	---	System 1 w/5 gpt reducing agent, 1 gpt catalyst and 10,000 ppm total iron w/900 psi CO_2
30	No	---	---	System 1 w/6 gpt reducing agent, 2 gpt catalyst and 10,000 ppm total iron w/900 psi CO_2
---	---	Stable	Yes	---

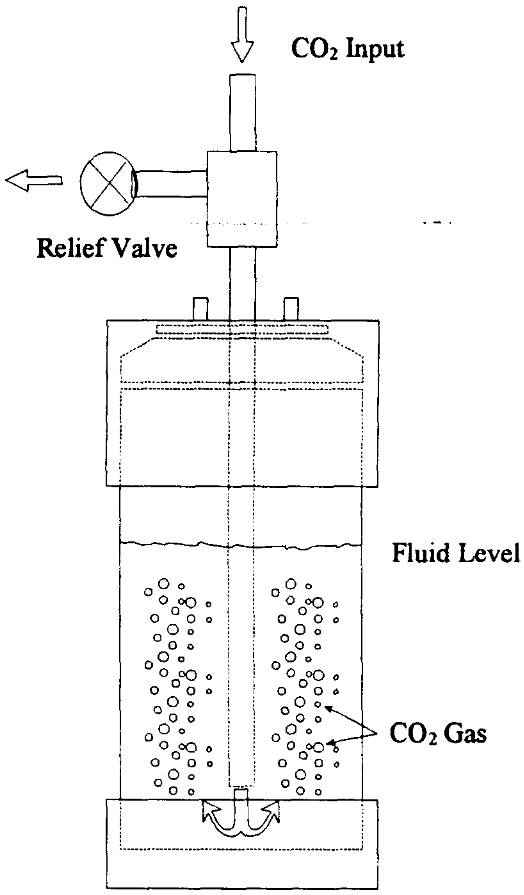

Figure 1 - Baroid 500 mL Corrosion Test Cell