SECTION C, PHYSICAL SCIENCES

Di-Metallic Polyphosphates Placed In Producing Zones of Oil Wells During Fracturing Minimize Scale Deposits

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The use of molecularly dehydrated phosphates to control the formation of scale has become increasingly popular in recent years. Condensed glassy phosphates control deposition in scaling waters, an effect which has become known as the "Threshold Treatment" (Hatch and Rice 1939, Rice 1941). The effectiveness of the "Threshold Treatment" is due to the surface-active properties of the complex phosphate ions, which reportedly become attached to submicroscopic crystals of potential scaling material and stop their growth. The effect can be demonstrated to some extent in the laboratory by the production of malformed crystalline growths from solutions containing complex phosphates (Jessen and Battle, 1943; Burcik, 1954). The di-metallic polyphosphates which contain oxides of calcium, zinc, strontium, barium, magnesium and aluminum combined in varying percentages with sodium oxide and phosphorus pentoxide have gained in importance since their early investigation in 1938 (Drynine, 1938; Yuster, 1939).

Scale deposits in oil wells have been a problem in certain areas for many years, and have caused expensive workovers. This scaling takes place in the tubing, downhole equipment, perforations or well bore, and in the formation itself. Some of the most common scales found in the wells are calcium carbonate, calcium sulfate, and barium sulfate. Some of these scales can be removed by chemical means, but others require mechanical removal.

The first use of the condensed phosphates was to either feed the material down the well bore or run a solution of the material down the annulus. The markedly smaller solubility rate of certain di-metallic polyphosphates opened another area of application in the oil-producing field. Owing to their slow rate of solution in water, such materials could be "dumped" in the well to protect downhole equipment. More recently, "by-passing" part of the produced water through such materials and back into the wells has been very effective. This method gives the operator much better control of the process.

Now, the combination of fracturing technique with the unique properties of di-metallic polyphosphates has made it possible to "condition" the water in the oil reservoir under essentially reservoir conditions. Thus, for the first time, it is possible to prevent scaling within the formation as well as on downhole equipment.

For use in conjunction with the fracturing technique certain properties are desired, and a determination of those properties were made on many di-metallic polyphosphates which are commercially available. These properties are: (1) high P_2O_5 content; (2) low solubility rate; (3) small particle size range; (4) slow reversion to orthophosphate; (5) slow reprecipitation.

Since the P_2O_5 content is a measure of the active part of the compound as far as the scale-inhibiting properties are concerned, the P_2O_5 content should be high. A high P_2O_5 content does not necessarily make a di-metallic phosphate adaptable, but it is of definite economic importance. Table I gives the P_2O_5 content of some materials.

TABLE I. Typical P_2O_5 Contents of Some Polyphosphates

	Per Cent P_2O_5 by Weight
Sodium-Calcium Polyphosphate	69
Sodium-Magnesium Polyphosphate	62 - 66
Sodium Hexametaphosphate (Commercial)	67
Sodium Tripolyphosphate	57.9
Sodium Pyrophosphate	53.4

The solubility rate is another of the properties of the polyphosphates which need consideration. If the material dissolves too rapidly, it increases the cost and/or reduces the length of time of effective treatment. Table II shows a comparison of rates of solution of four samples of di-metallic polyphosphates mixed with 9 parts by weight of 20-40 Ottawa-type sand.

TABLE II. Rate of Solution of Polyphosphates. Distilled Water @ 75°F.

		P_2O_5 in effluent ppm				
Type Polyphosphate	Flow Rate, cc/min.	1 Wk.	2 Wk.	3 Wk.	2 Months	3 Months
Sodium-Calcium - A	2	65	65	65	25	13
Sodium-Calcium - B	2	85	470	40	35	Trace
Sodium-Magnesium - C	2	1200	30	0	0	0
Sodium-Magnesium - D	2	130	125	2	0	0

Other factors besides the type of polyphosphate which affect rate of solution are particle size (surface area), type of water produced, and temperature. Of these factors, generally only particle size can be controlled. Smaller particles have a greater surface area per pound, resulting in a faster solution rate. Normally, there is an upper limit of particle size that can be placed during a fracture treatment. When a phosphate is employed in conjunction with fracturing, a balance between solution rate and particle size is beneficial. A small particle size range with a minimum of fines is desirable.

Slow reversion to orthophosphate is another of the desired properties (Bell, 1947; Green, 1950). This is important, as the calcium ions form a precipitate with the orthophosphate ions, which would be detrimental to the producing zone. After the elimination of the di-metallic polyphosphates having rates of solution definitely too high, the reversion rates of the remainder were satisfactory for this usage.

Any chemical placed in a fracture should not react with the produced water or with the formation to form a precipitate or an insoluble complex. This could result in a plugging action, defeating the purpose of the treatment. Figure 1 shows excellent examples of what can happen when some polyphosphates contact a brine solution. The four graduated cylinders each contained a clear 50 ppm. solution of a different di-metallic polyphosphate and the beakers contained identical clear salt-water brine. The polyphosphate solutions were added to the respective beakers of brine and stirred. After one hour a large amount of precipitate could be observed in C and D and a slight cloudiness in B, while A remained perfectly clear.

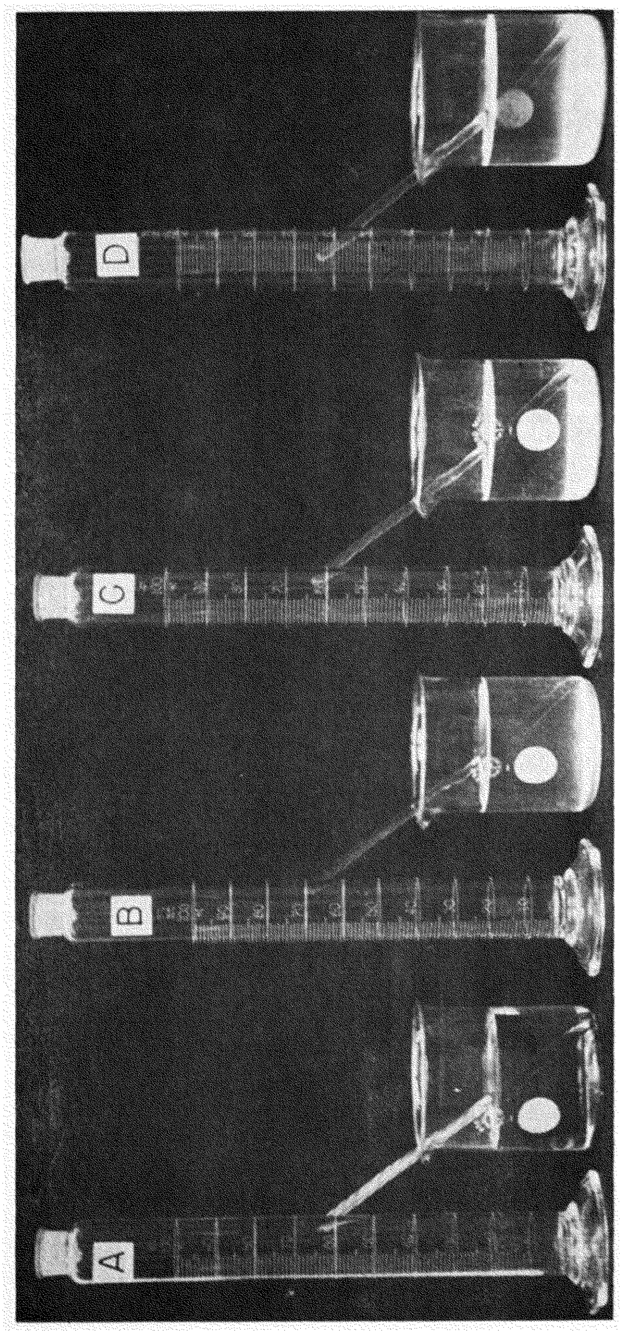

Figure 1. Precipitation Tests:
Precipitate allowed to settle for one hour.
Cylinder A Sodium calcium polyphosphate A
Cylinder B Sodium calcium polyphosphate B
Cylinder C Sodium magnesium polyphosphate C
Cylinder D Sodium magnesium polyphosphate D

This precipitation also can occur in distilled water, as shown in Table III.

Table III. Precipitation at 160°F. in Distilled Water

Di-Metallic Polyphosphate	Time to precipitate at 160°F. (Distilled water).
Sodium-Calcium - A	None after 7 days
Sodium-Calcium - B	3 hours
Sodium-Magnesium - C	21 hours
Sodium-Magnesium - D	18 hours

Generally, the formation water would be produced from the well in a few hours to a few days depending on the proration schedule.

Any material used in this type treatment should neither soften when contacted by water nor absorb water so as to result in a thin gel-like layer being formed over the particles. Either of these conditions may cause rapid depletion of the polyphosphate.

Field Applications. Many treatments of oil wells using this technique have been made with very successful results.

One well owner reported a net gain of approximately 9,000 barrels of oil during a six-months period from six wells after placing 200 to 600 pounds of a sodium-calcium polyphosphate in each. During that interval, production was uninterrupted by scaling and was still higher at the end of that time than before treatment.

A well in West Texas treated with 200 pounds of phosphate over a year ago still has active P_2O_5 and has had no scale problems. Six months after treatment, tubing and pump were pulled for inspection and no scale was observed. An offset well not treated has had very serious scaling trouble.

Production on a well in Wyoming was following normal expected decline until a deposition of calcium carbonate began forming, at which time the production curve dropped very sharply (See Figure 2). A 500-gallon 15 per cent acid wash gave very little assistance. After treating with a fracturing-polyphosphate combination, production increased to over 100 barrels oil per day. The production curve appears parallel to but is higher than that prior to scaling.

These are, of course, just a few examples of the effectiveness of this type of treatment.

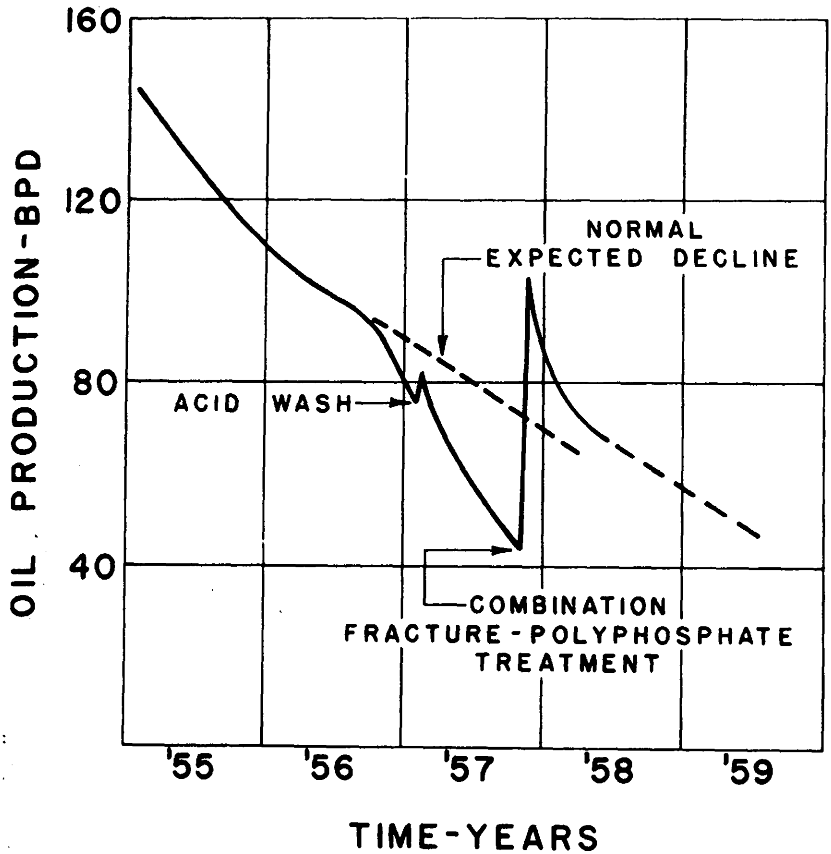

Figure 2. Oil Production, Well "A", Wyoming.

Summary and Conclusions. A procedure for checking scale deposition in the producing formation as well as in the well bore, tubing and producing equipment has been introduced to the oil industry. Field experience has shown the combination of fracturing with polyphosphate treatments to be an economical, long-lasting technique for inhibiting scale in many wells where frequent shut-downs had been common.

Several di-metallic polyphosphates are available for this type treatment, but to obtain the most economical scale inhibition several factors should be considered in making a selection. Both laboratory and field experience give strong evidence that some sodium-calcium polyphosphates possess a maximum number of desirable characteristics.

LITERATURE CITED

Drynine, P. D. 1958. Mineralogy of Water Flooding. Prod. Monthly. December.

Yuster, S. T. 1939. The Gypsum Problem In Water Flooding. Prod. Monthly. April 27.

Hatch, G. B., and Rice, Owen. 1939. Surface Active Properties of Hexametaphosphate. Industrial and Engineering Chem. 31: 51.

Rice, Owen. 1941. Plant Results with Threshold Treatment. Second Annual Water Conference, Pittsburgh, Pa., November 3-4.

Jessen, F. W., and Battle, J. L. 1943. Brine Stabilization with Sodium Hexametaphosphate, Industrial and Engineering Chem. 35: 650.

Burcik, Emil J. 1954. The Inhibition of Gypsum Precipitation by Sodium Polyphosphates. Prod. Monthly, November: 42.

Bell, Russell N. 1947. Hydrolysis of Dehydrated Sodium Phosphates, Industrial and Engineering Chem. 39: 136.

Green, Jerome. 1950. Reversion of Molecularly Dehydrated Sodium Phosphates, Industrial and Engineering Chem. 42: 1542.