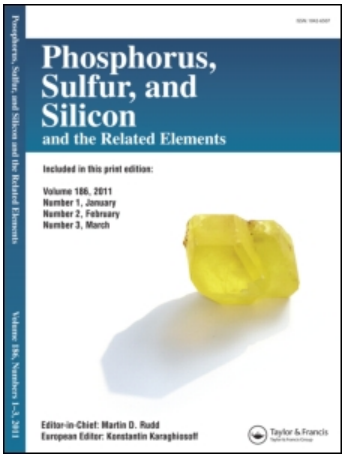

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TECHNICAL AMINOPOLYMETHYLENEPHOSPHONIC ACIDS AS SCALE INHIBITORS

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Abstract Aminopolymethylenephosphonic acids are complexing agents which can easily be synthesized technically and which, referring to their strong threshold effect, are used to a large extent as scale inhibitors. As a consequence of their increasing use, especially in the oil industry, they now represent the largest group of commercially available phosphonates

TEST METHODS

A number of easy and practice-related test methods have been developed for the characterisation of their complexing ability and scale-inhibiting properties. The Hampshire test makes use of a titration of a sodium carbonate phosphonate solution with a calcium salt solution until precipitation of calcite occurs. In contrast, in the modified Hampshire test, freshly precipitated calcite is dissolved by the addition of complexing agents. Besides, the inhibition of calcite-, gypsum- and baryte scale is determined according to an internationally common static test (72 h) as well as according to a mixed dynamic (= 24 h)/static (= 16 h) method under different pH- and temperature conditions and at different foreign electrolyte concentrations. In the exclusively dynamic test, synthetic North Sea water is pumped through a steel capillary at 70 and

90 °C, and the pressure increase resulting from a constriction of the steel capillary as a result of scale formation is measured.

TEST RESULT

The values established by means of the Hampshire test show that the complexing ability in mg $CaCO_3$/g acid does not correlate with the number of methylenephosphonate (= mpa) groups:

Amino $(mpa)_3$	820
Ethylenediamine $(mpa)_4$	1000
Diethylenetriamine $(mpa)_5$	1020
Bis(hexamethylene)triamine $(mpa)_5$	230
Hydroxyethylethylenediamine $(mpa)_3$	> 2500
Hydroxyethylethylenediamine $(mpa)_{2-3}$	> 5000

The effect of the pure hydroxyethylethylenediamine $(mpa)_3$ is even exceeded by that of mixtures of bis- and tris(methylenephosphonic acid).

Test-Method	Dynamic		Dynamic/Static		Static				Dynamic/Static		Static		
Scale-Medium a)	GYPSUM (5.0 g/l)		GYPSUM (12.0 g/l)		GYPSUM				CALCITE (0.25 g/l)		CALCITE (4 g/l)		
					5 g/l		9 g/l						
Foreign Electrolyte Conc. (g/l)	7.5		10.3		11.9		15.3		30		33		
pH	6.4		6.2		6.0		6.0		9.5		7.3		
Temperature (°C)	90		70		70	90	70	90	85		70		
Inhibitor / ppm	1	3	30	40	1	5	20	20	2.5	5	10	20	40
Amino $(mpa)_3$	83	100	42	44	92	94	98	23	100	100	67	85	92
Ethylenediamine $(mpa)_4$	96	100	90	100	99	100	100	12	93	100	65	86	88
Diethylenetriamine $(mpa)_5$	100		100	100	100	100	100	100	100	100	66	95	100
Bis(hexamethylene)-triamine $(mpa)_5$	100		100	100	100	100	100	55	100	100	66	91	100
Hydroxyethylethylene-diamine $(mpa)_{2-3}$	55	95	34	75	39	95	94	3	90	100	52	79	100
Hydroxyethylethylene-diamine $(mpa)_3$	30	61	27	61	20	90	71	3	84	100	48	62	92
Hydroxyethanediphosphonic acid (to comparison)	24	48	0	0					100	100	90	100	100

Table 1 Inhibition under different conditions

a) total amount of GYPSUM or CALCITE resp. resulting from Ca^{2+} and equivalent amounts of sulfate or carbonate respectively

Table 1 summarizes examples of scale inhibition under exclusively static, mixed static/dynamic and exclusively dynamic conditions. In the static test all aminomethylenephosphonic acids give excellent inhibition results at 70 °C towards $CaSO_4$ scale. At 90 °C and 9 g $CaSO_4$/l, diethylenetriamine(mpa)$_5$ proves to be the most effective representative of this product group. Over a pH-range from 4 to 10 as well, this compound inhibits $CaSO_4$ formation (5 g/l) completely at 90 °C at concentrations from 3 ppm onwards, followed by bis(hexamethylene)triamine(mpa)$_5$. Ethylenediamine (mpa)$_4$ has an optimum effect at pH 4-6, and amino(mpa)$_3$ displays an increasing inhibition effect from pH 4 to 10.

Under mixed dynamic/static and also under exclusively dynamic test conditions, both penta(mpa) compounds display the best inhibitive effects. Although bis(hexamethylene)triamine(mpa)$_5$ displays the lowest complexing ability, its inhibitive effect exceeds that of most other aminomethylenephosphonic acids. Under dynamic/static conditions all aminomethylenephosphonic acids inhibit calcite scale formation completely from 5 ppm onwards at pH 9.5 and also at a very high electrolyte concentration. The test results obtained under static conditions show that, at higher calcite concentrations (4 g/l), it is again the (mpa)$_5$ types and also the bis/tris(methylenephosphonic acid) mixture that prove to be the most effective inhibitors for complete scale inhibition.

SYNERGISTIC EFFECTS

A remarkably high degree of baryte scale inhibition can be attained when using aminomethylenephosphonic acids in combination with low-viscosity polyacrylate

types:

Hydroxyethylethylenediamine(mpa)$_{2-3}$	40 % inhibition
Polyacrylate (viscosity < 10000 mPa)	49 % inhibition
Mixture, weight ratio 1:1	100 % inhibition

MANUFACTURING

Aminomethylenephosphonic acids are synthesized from the corresponding amine, phosphorous acid and formaldehyde in the presence of hydrochloric acid. In this reaction, exhaustive methylenephosphonylation only takes place if adequately high hydrochloric acid concentrations are present (Fig. 1). To achieve the technically desired optimum effectiveness of the bis/tris (methylene phosphonic acid) mixture, a mole ratio of amine to HCl of 1:1 is required.

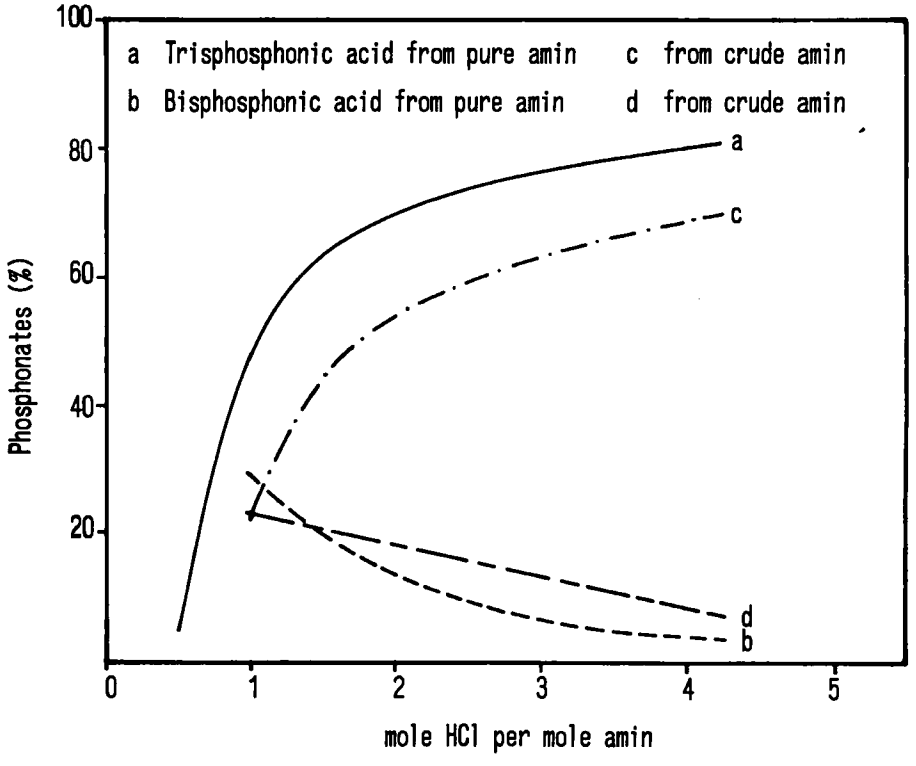

Fig.1: Formation of Phosphonates vs. Excess of HCl