Dissolvine® in Oil Field and Allied Applications

Reference:

A major problem encountered in oil field operations is the occurrence of scale both downhole and in pipelines. As the formation of scale causes blocking, scale problems invariably lead to loss of oil production. Oilfield installations, particularly the offshore ones, are extremely expensive. Therefore effective scale removal is of paramount importance.
The scales usually consist out of water-insoluble salts, typically carbonates and sulphates of magnesium, calcium, strontium and barium. A very common constituent of scales are iron oxides. Traces of many other metal salts may be encountered as well.

Carbonate Scale Removal

Generally, carbonate scale can be removed very efficiently by hydrochloric acid and by chelating agents, the latter agent having the advantage of low corrosion and no uncontrolled evolution of carbon dioxide gas.
Should a hydrochloric acid treatment be followed by an aqueous EDTA solution, it is recommended to use the ammonium form of EDTA (Dissolvine AM2-40, AM2-45 or AM3-40) rather than the sodium form (Dissolvine E-39) as the latter may give rise to precipitation of insoluble EDTA-acid.

Sulphate Scale Removal

Contrary to carbonate scales, sulphate scales cannot be removed by an acid treatment. To attack the latter scales, including barium scales, formulations containing chelating agents have proved to be very efficient. A key-factor for successful removal of oil-field scales is the rate of dissolution. Not only does the type of chelating agent play an essential role, but also the pH, solution concentration and the presence of special additives can be important.
The main-types of chelating agents used for sulphate scale removal are EDTA and DTPA. Both can form very stable chelates with alkaline earth metal ions. The optimum value for the pH is generally between 8 and 12. In Table 1 stability constants (log-values) are listed for the alkaline earth metal chelates of EDTA and DTPA.

Table 1: Stability constants
LogK values

Metal ion	EDTA	DTPA
Mg^{2+}	8.8	9.3
Ca^{2+}	10.7	10.8
Sr^{2+}	8.7	9.8
Ba^{2+}	7.9	8.9

Table 1 indicates that for calcium both EDTA and DTPA give rise to equally stable chelates, whilst in the case of barium DTPA forms a more stable chelate than EDTA. This is well in line with what is usually observed in practice. Generally speaking, calcium scales are more effectively and cheaply removed by EDTA-containing formulations, whilst in the case of barium scales DTPA is to be greatly preferred.

Counter-ions

The standard products in our Dissolvine range usually contain sodium as counter ions to neutralise the carboxylate groups present in EDTA and DTPA. They are available as aqueous solutions (39% for EDTA-Na4 and 40% and 50% for DTPA-Na5) under the trade names Dissolvine E-39 Dissolvine D-40 and Dissolvine D-50, respectively.
Chelating agents carrying other counter-ions, like ammonium or potassium, need more elaborate methods of production and are consequently higher in price.
The type of counter ion has a significant effect on the solubility of the metal chelate. Generally speaking, metal chelates carrying sodium counter-ions are much less soluble than the corresponding ammonium or potassium forms.
Under oil field stimulation conditions, in particular for removing barium and strontium scales, the potassium forms of EDTA and DTPA have been shown to be especially effective. They are much more effective than the corresponding ammonium and far more effective than the corresponding sodium forms.

Iron Containing Scales

When scales contain iron, problems may arise due to the precipitation of ferric hydroxide. Iron can be present either as ferrous (Fe^{2+}) or as ferric (Fe^{3+}) ions. In contact with air, however, the ferrous ions are invariably oxidised into the ferric form, which gives rise to ferric hydroxide precipitate above a pH-value of 3.
In typical scales, iron often occurs as ferrous sulphide (FeS). This insoluble salt is readily dissolved in concentrated acid, but upon neutralisation iron hydroxide starts to precipitate out. That is why the use of ammonium EDTA can be beneficial, because it prevents the formation of insoluble EDTA-acid. Also the use of HEDTA (Dissolvine H-40) can be helpful in this aspect.

Dissolvine Products and Effect on pH

When Dissolvine E-39 is diluted with demineralised water (1:100 v/v), the pH will be around 11.3, so relatively small amounts of this product can have a significant impact on the pH of aqueous solutions to which it has been added: The pH is easily raised by several units.
This pH-raising effect is virtually absent with the aqueous solutions (40% m/m) of di- and tri-ammonium EDTA (Dissolvine AM2-40, AM2-45 and AM3-40). Upon 100 times dilution these products display a pH of 5 and 7, respectively.
The same holds for Dissolvine NA2. This crystalline powder gives a pH of 4 to 5 upon dissolving (1%) in water.

Summary of Dissolvine Characteristics in Oilfield Applications

Dissolvine E-39 **Dissolvine 100-S**	EDTA-Na_4, 39% aqueous solution Standard EDTA product, suitable for removing calcium and strontium scales.
Dissolvine NA	EDTA-Na_4, micro-granular powder, assay 86% Standard EDTA product, suitable for removing calcium and strontium scales, gives flexibility in making up solutions of different concentrations.
Dissolvine NA-X **Dissolvine 220**	EDTA-$Na_4.4H_2O$, crystalline, non-dusty product Contains less than 0.1% NTA (as NTA-H_3), suitable for removing calcium and strontium scales.
Dissolvine NA2	EDTA-$Na_2H_2.2H_2O$, crystalline product Low impact on pH upon dissolving in water, suitable for removing calcium and strontium scales.
Dissolvine Z	EDTA-H_4, crystalline product, insoluble in water The free acid form of EDTA, can be converted with potassium base into a highly effective agent for removing calcium and strontium scales.
Dissolvine AM2-40 **Dissolvine AM2-45**	EDTA-$(NH_4)_2H_2$, 40% or 45% aqueous solution Slightly acidic upon dissolving in water, very effective against iron-containing scales.
Dissolvine AM3-40	EDTA-$(NH_4)_3H$, 40% aqueous solution Almost neutral upon dissolving in water, very effective against iron-containing scales.
Dissolvine H-40	HEDTA-Na_3, 40% aqueous solution Standard HEDTA product, suitable for iron scales, does not form a solid precipitate in contact with strong acids.
Dissolvine D-40 **Dissolvine D-50**	DTPA-Na_5, 40% or 50% aqueous solution Standard DTPA product, suitable for removing strontium and particularly barium scales.
Dissolvine D-88	DTPA-Na_5, micro-granular powder, assay 88% Standard DTPA product, suitable for removing strontium and particularly barium scales, gives flexibility in making up solutions of different concentrations.
Dissolvine DZ	DTPA-H_5, crystalline product, insoluble in water The free acid form of DTPA, can be converted with potassium base into a highly effective agent for removing strontium and particularly barium scales.
Dissolvine D-K5-40	DTPA-K_5, 40% aqueous solution Specialised DTPA product, especially recommended for barium and strontium scales.

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Recommendations for Dissolvine Usage

With alkaline earth scales, **EDTA** is most effective for **calcium**, whilst the larger molecule **DTPA** is to be preferred for **barium**. With strontium both EDTA and DTPA can be used.
The most common form of our Dissolvine chelating agents (i.e. E-39, 100-S, NA, NA-X, NA2, H-40, D-40, D-50 and D-88) contain sodium as the counter-ion.
However in barium and strontium scale removal the **potassium** forms i.e. potassium-EDTA (strontium) and potassium-DTPA (barium) are far more **effective** than the sodium forms.
The potassium forms can be prepared from the corresponding free acids i.e. Dissolvine Z (EDTA-H4) and DZ (DTPA-H5), respectively.
Carbonate scales of the alkaline earth metals can be treated with hydrochloric acid and chelating agents. However for removal of the sulphate scales the use of chelating agents is necessary.
Should a hydrochloric acid treatment be followed by a formulation containing a chelating agent, one should take care to avoid precipitation of the chelating agent in its free acid form. Therefore the use of Dissolvine AM2-40, AM2-45, AM3-40 or H-40 is recommended

Further Information

For transport, handling and first aid instructions please refer to the Safety Data Sheet, which is available on request.
For samples, technical service and further information, please contact your nearest Akzo Nobel Chemicals Sales Office or agent, or: