GENESYS INTERNATIONAL

AG1 – WWRO Antiscalant replaces acid dosing

Extract from the paper "Theoretical and practical experience of calcium phosphate inhibition in waste water RO plant", presented at the IDA World Congress on Desalination and Water Reuse at Maspalomas, Gran Canaria, Spain, 21-26 October 2007.

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Genesys PHO has been found to reduce or eliminate the need for acid dosing in high phosphate reverse osmosis feed waters, such as surface and tertiary effluent, while controlling the potential for calcium phosphate scale deposition.

Application

There has been an increasing trend over the last 10 years to treat and reuse waste water for industrial supplies, irrigation, aquifer recharge and drinking water as in the NEWater projects in Singapore. The reduced energy consumption due to lower pumping costs makes this approach up to 50% cheaper than desalting seawater. Waste water such as municipal effluent and agricultural run-off can have very high phosphate levels which results in the formation of calcium phosphate scaling on membrane surfaces. This has been confirmed during membrane autopsy procedures. In the past, antiscalant chemistry based on threshold inhibition and crystal distortion has had poor results in high phosphate/high pH waters. The alternative of dosing large quantities of acid to lower the scaling tendency is no longer an acceptable approach for environmental, safety and cost reasons. In 2005 Genesys started some project work to investigate the chemistry of calcium phosphate. Laboratory and pilot plant testing resulted in the successful formulation of a new calcium phosphate antiscalant.

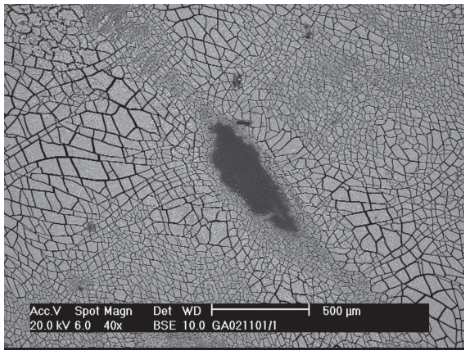

Fig 1: Calcium phosphate amorphous deposit

Reducing the pH from 7.5 to 6.0 on a 2,700 m³/day plant would require over 1-1.5 tons of sulphuric acid per day. Handling this quantity of acid is an environmental, health and safety and logistical problem that many plant operators would like to avoid whenever possible.

Phosphate Chemistry

Phosphate is a salt of phosphoric acid. The phosphate ion is polyatomic consisting of one central phosphorous atom surrounded by four identical oxygen atoms in a tetrahedral arrangement. The phosphate ion carries a negative three charge and can exist in the following forms in solution as pH becomes increasingly acidic:

Phosphate ion – PO_4^{3-}
Hydrogenphosphate ion – HPO_4^{2-}
Dihydrogenphosphate ion – $H_2PO_4^{-}$
Phosphoric acid – H_3PO_4

It is a hypervalent molecule as the phosphorous atom has 10 electrons in its valence shell. There are many types of phosphate salts all with different solubilities and all potentially forming at the same time in a membrane system. The majority of calcium phosphate deposits are amorphous and only two forms, hydroxyapatite and fluoroapatite, take on a crystalline structure. *Figures 1* and *2* show calcium phosphate deposited on a membrane. Hydroxyapatite is rare and only formed in this case because an electricity shutdown left the super saturated solution present in the membrane for four days without flushing.

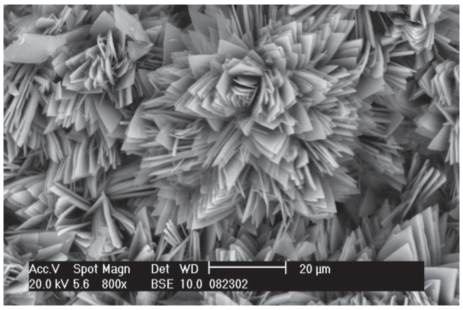

Fig 2: Calcium hydroxyapatite crystals

Calcium Phosphate Deposition Mechanisms

Calcium orthophosphate deposition mainly occurs in the last membrane of the last stage of the RO plant where the concentration of ions is at its highest. An insoluble, very thin 50 – 200 µm amorphous non crystalline mat can build up rapidly, reducing permeate flow by 20 – 40 % in only two hours. In the initial stages of precipitation and deposit formation calcium phosphate can be taken back into solution by acid dosing. However, deposits form rapidly and the feed spacer can quickly become blocked making cleaning impossible because there is insufficient flow across the membrane surface.

Mode of Action

The product investigation concentrated on increasing the threshold inhibiting effect of a phosphonate inhibitor by using a synergistic blend of organic chemicals. The presence of crystalline calcium phosphate is so rare that the use of crystal distortion chemicals was ignored. Threshold inhibition prevents the ionic ordering and nucleation stage of precipitation (*Figure 3*) thus allowing the calculated solubility of ionic solutions to be exceeded.

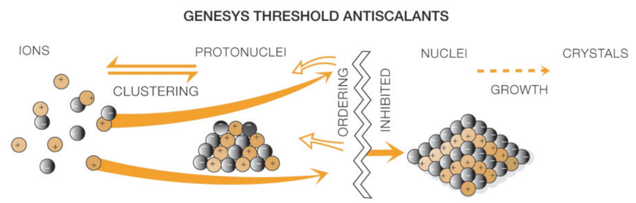

Fig 3: Threshold Inhibition mechanism

Pilot Study, Alicante, Spain

Brackish Water RO Plant Data

- Product Flow 132m³/hr Recovery 70%
- Raw Water pH 7.2-8.2 Temperature 25°C
- Calcium 160mg/l Silica 13mg/l
- Bicarbonate 401mg/l Sulphate 290mg/l
- Iron 0.05mg/l Chloride 445mg/l
- TDS 1691mg/l Phosphate 19mg/l
- Feed Pressure 10 bar Nitrate 0.5mg/l

Acid Dosing & Conventional Anti-Scalant

Figure 4 below shows the performance of conventional antiscalants C, A and the Genesys PHO (Antiscalant B) calcium phosphate specific antiscalant. The use of conventional antiscalants did not control calcium phosphate scaling. At a pH of 7 and above membrane fouling occurred and the plant needed to be shut down and acid cleaned. When acid was dosed to a pH of 6.2 and conventional antiscalants used then fouling was controlled. To reduce the pH to 6.2, hydrochloric acid at 66 kg per day was required.

Control with Genesys PHO

Genesys PHO was initially dosed at 4mg/l with acid dosing to pH of 6.2. Gradually the acid dose was reduced and then the antiscalant dose reduced from 4 to 2mg/l. Throughout this period there was no change in flux or pressure indicating fouling was being prevented. This saved 23,000 kg of hydrochloric acid per year and the logistical, environmental and health and safety issues associated with handling acid.

Output	20,000m³/day	95% Sulphuric Acid Dose	123mg/l 5,629kg/day
Recovery Rate	85%	Sulphuric Acid Cost/year	$822,000
Treated effluent pH	7.5	Phosphate Antiscalant dose/day	3mg/l 70kg/day
Feed water pH	6.0	Phosphate Antiscalant cost/year	$255,000
Phosphate levels	25 mg/l	**SAVINGS/YEAR**	**$567,000**
Calcium	200 mg/l		

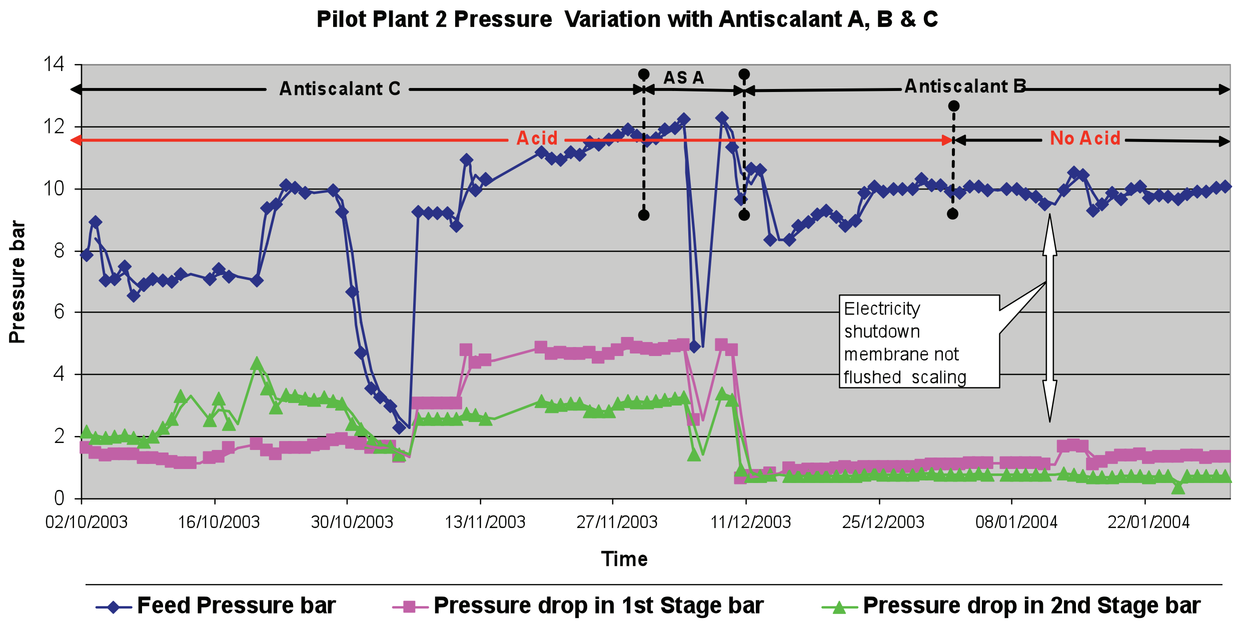

Fig 4: Conventional antiscalant performance and Genesys PHO (antiscalant B)

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