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Modeling and Management of Scale Potential in an Oil Field Production Network

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ABSTRACT

Diversity and complexity of chemical treatment operations provide difficulties to evaluate an impact of chemicals used for solving different production issues. Integrated chemical management system will provide a better understanding and evaluation of chemical performance. Some chemical treatment modeling software is available on the market with capabilities to simulate and evaluate particular production issue. Unfortunately they are not able to cover majority of issues under one application. Approach to integrate chemical applications by using asset integration software called “Pipe-It” based on example of created scaling potential management models in an oil field production network was proposed and discussed under this work, which mainly consists of three parts.

First chapter highlights theory and chemicals used to solve main production issues appeared during production operations at one of the Norwegian Continental Shelf (NCS) oilfields. Theory behind each issue is stated. General types of chemicals used for treatment operations in oil and gas industry, their features and appreciation on the production of oil and gas are shown and summarized at Appendixes A-G.

Second part of work is devoted to description of chemical treatment system used at one of the oilfields located at NCS. Main facilities and associated production streams (three-phase flow, oil, gas and water) are shown. Chemicals associated with these streams are highlighted for each platform. Chemicals injection points are shown for one production and one processing facilities.

Last chapter describes implementation of computational models for tracking of scale potential in oilfield production systems within Pipe-It. Oddo-Tomson calculations were used to evaluate precipitation potential of barium sulfate scale. Models were adapted for assumed production system of Ekofisk production platform X and were built within table and visual format. They were called “table case” and “visual case” respectively. Self-triggering model for monitoring scaling potential within wells and production manifolds was created and described at chapter three.

Results of the work show effective, fast and robust way to implement different chemical treatment models based on example of scale potential monitoring system integration. Visualization is one the advantages of Pipe-It integration approach providing a value for better understanding of chemical treatment applications used for actual production operations at particular facility and as well as the asset level.

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INTRODUCTION

Chemical treatment operations are necessary to maintain sustainable hydrocarbon production at oil, gas or gas condensate fields. Hydrocarbons coming out of a reservoir consist of hundreds of different components (N_2 , CO_2 , H_2S , C_1 - C_6 , C_7+ , etc.) and may present in a liquid (C_{5+}) or gaseous form (C_1 - nC_5). In addition water is usually associated to hydrocarbons coming out of reservoir, bringing within itself to the surface various dissolved compounds: formation ions, bacteria, solids, etc. Resulting composition of producing fluid may count up to large number of different components and substances.

As these fluids will experience drop in pressure or a change in temperature, some compound may become, for example, more stable at solid state and will start to precipitate leading to unpredictable changes influencing overall production. These effects are summarized under the term production issues or problems.

Physicochemical changes lead to occurrence of production (deposition of scales, corrosion products, wax, asphaltenes, hydrates) or processing (foaming, emulsion stabilization, etc.) issues. Produced streams are mixed within production manifolds during further transportation to processing units. At each mixing point new fluid composition and conditions may bring more problems to production process. That is why it is really necessary to monitor production conditions and composition of produced fluids at each point in order to predict occurrence of particular problem.

When various problems, such as: scaling, corrosion, biofouling, foaming, emulsification, etc., are predicted or detected during upstream operations, they can be solved by application of different chemical and nonchemical techniques. First method uses chemical treatment providing impact on composition of the fluid, therefore preventing or mitigating particular problems. Second method varies physical parameters of the flow (temperature, pressure, rate, etc.) to provide the similar impact.

Many reagents used for solving particular issue sometimes have a significant impact on performance of others chemicals. That is why they should be carefully chosen by chemical supplier and production chemists before being applied at the field. Production chemistry issues ought to be determined during the field development stage by the operator company, often in collaboration with vendors - service companies, to find out the best solutions.

Next chapter highlights main production issues occurred during oilfield production experience of one of NCS oilfield. That field and chemical treatment operations used to overcome production problems will be described further at chapter two. General chemical types utilized in oil and gas industry are summarized at Appendixes A-G.

1 PRODUCTION ISSUES

To prevent production issues it is possible to act upon two types of parameters: physical (pressure, temperature and rate) or chemical (composition of fluids) conditions. Fluids coming out of the reservoir have their own composition which can be easily modified by adding properly selected chemical additives to prevent issues described before, meanwhile physical parameters are mainly dependent on reservoir conditions and therefore nonchemical techniques can be applied to vary streams physical conditions. Among them many methods are available to prevent production issues. Some parts of them are summarized under Table 1.

<u>#</u>	<u>Issue</u>	<u>Method</u>
1	Scaling	Increase pressure, decrease temperature (depends on particular scale)
2	Corrosion	Corrosion-resistant materials and coatings
3	Biofilm	Increase turbulence
4	Foaming	Decrease flow rate
5	Emulsification	Insulation, pipeline heating and in separator, decrease flow rate, use electric fields, centrifugation
6	Removal of solids, fines and specific ions	Membranes and fine filters, pigging of pipelines, scraping tools, milling or drilling/reaming

In general, methods listed above are not providing sufficient results to be applied independently; therefore they are usually utilized in combination with chemical applications overcoming or minimizing the effect of production and processing issues. Substances used for chemical treatment operations may be classified as:

- Inhibitors to mitigate fouling and corrosion;
- Solvents to remove precipitated or deposited solids;
- Chemical aids to maintain and improve hydrocarbon separation processing;
- Supporting chemicals added for some other benefit, including environmental compliance.

To act against production problems it is necessary to understand mechanism of these processes, its resources and conditions when they can appear. Next sections highlight main production issues and types of chemicals used for treatment operations. The effect and features of general chemical types utilized during production of oil and gas are shown and summarized at Appendix A-G.

1.1 Scaling

Fouling (scaling) is the accumulation of unwanted material on solid surfaces to the detriment of equipment functioning (Wikipedia, 2013). For example, limescale (calcium carbonate) deposited inside a pipe has two major effects: first, it reduces liquid flow through the pipeline; secondly, it reduces thermal conductivity to the outer pipeline shell. Both effects will reduce the overall thermal efficiency if pipe should be used as a heat exchanger. An example of scaling is shown at Figure 1.1.



Figure 1.1 - Limescale build-up inside a pipe

Scale formation in water with high mineral content can reduce the production capacity of the wells and shorten the life time of equipment – both topside and downhole. There are several mineral ions usually dissolved at produced water: calcium (Ca^{2+}), barium (Ba^{2+}), strontium (Sr^{2+}) cations and carbonates (CO_3^{2-}), sulfate anions (SO_4^{2-}). Due to temperature and pressure variations (buildup, reduction or sudden drops), commingling of incompatible water streams and also pH changes, water solution can become supersaturated. The term supersaturation refers to a solution that contains more of the dissolved material than could be dissolved by the solvent under normal circumstances (Wikipedia, 2013). Under these conditions mineral salts become less soluble and excess amounts of ions reacts, depositing out on a pipeline or equipment surface as a thick scale. The scale adsorbs onto imperfections of pipeline walls, downhole equipment, and on the walls of wellhead equipment hereby reducing production rates, jamming critical isolation or safety valves and causing well instrument lines to plug.

Oil and gas industry has experienced scaling problems in various circumstances. Statoil published brief description of their experience of scaling deposition during various operations (Statoil, 2007):

- Drilling and well completion. If the drilling mud or completion fluid is incompatible with the formation water;
- At the commissioning stage of new injectors. If injection water is incompatible with the formation water;
- During production. When a well starts to produce formation water with the hydrocarbons;
- During well stream processing, when significant quantities of produced water put process equipment at risk;
- Commingled production. Where well streams from various formations, reservoirs or individual wells are mixed together.

Next section will briefly describe scaling theory to provide understanding how can engineers influence on this process.

1.1.1 Scaling theory

As stated at previous sections temperature or pressure change, pH variations, or contacts with incompatible water are the driving forces of scale formation. Although many produced waters that became supersaturated do not always produce scale. As Schlumberger engineers stated at their report “Fighting Scale—Removal and Prevention” (Crabtree, et al., 1999), in order for a scale to form it must grow from solution. The first development phase within supersaturated water is a formation of unstable clusters of atoms, a process called homogeneous nucleation (Figure 1.2). Then clusters form a solid structure with imperfect surface where further growth is going on.

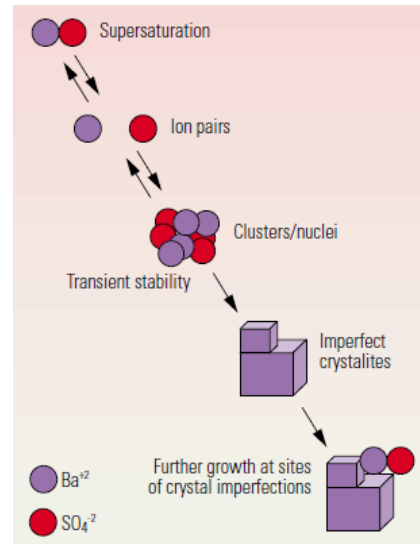


Figure 1.2 - Homogeneous nucleation mechanism by (Crabtree, et al., 1999)

American researchers also described at their work second mechanism of crystal growth called heterogeneous nucleation (Figure 1.3). Where scales deposition also tends to initiate on a preexisting fluid-boundary surface. Places where this type of nucleation appears include: (a) surface defects such as pipeline surface roughness or perforations in production liners, (b) joints and seams in tubing and pipelines. Highly turbulent flow can also catalyze scale deposition, so the accumulation of scale can occur at the places where the pressure is equal to the bubble point pressure. This is the reason why scale deposits rapidly on downhole completion equipment.

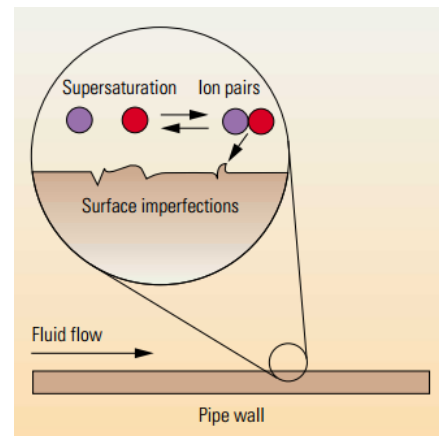
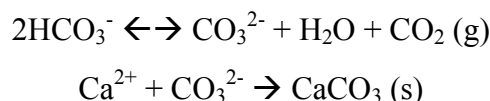


Figure 1.3 - Heterogeneous nucleation mechanism by (Crabtree, et al., 1999)

As stated above, scaling involves crystallization of solid salts; meanwhile other components such as oxides and hydroxides can be also deposited. These are most often water solutions, but non-aqueous precipitation fouling is also known (Kelland, 2009). There are several types of crystallization reactions occurring within water solution. As an example of the most prevailing salt at natural water, an equilibrium reaction between the readily soluble Ca(HCO₃)₂ (calcium bicarbonate) and the poorly soluble CaCO₃ (calcium carbonate) is shown below:



Reactions can be summarized under 1 equation:



As the result of reaction calcium carbonate precipitates. The volatility of CO₂ increases as the temperature grow within some process utilities, hence the scaling is higher at the hotter places of the processing units, than on cooler parts. For instance, more scaling occur at hotter outlet of heat exchanger than at the cooler inlet.

In general, scaling mainly depends on two driving forces: (a) the dependence of the salt solubility on temperature and (b) presence of evaporation. Various salts have different dependences of solubility on temperature: "normal" or "retrograde" types. Increased solubility with increasing temperature is referring to the salts with the "normal" type of solubility and thus will precipitate at the cooling surfaces. The salts with "inverse" or "retrograde" solubility will deposit at the heating surfaces. For instance, calcium sulfate is a common precipitation salt of heating surfaces due to its retrograde solubility.

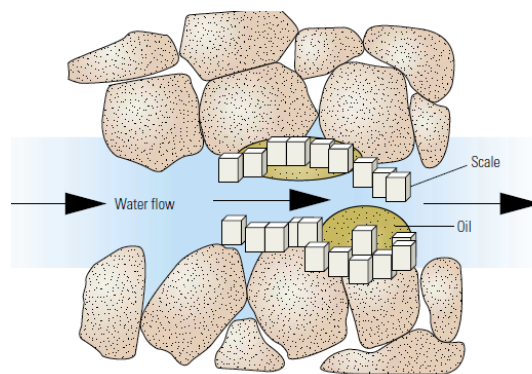


Figure 1.4 - Scaling damage within reservoir (Crabtree, et al., 1999)

TABLE 2 - COMMON SCALES

#	Name	Chemical formula	Mineral
1	Calcium carbonate	CaCO ₃	Calcite, aragonite, or rarely vaterite
2	Calcium sulfate	CaSO ₄	Anhydrite, hemihydrate (CaSO ₄ ·0.5H ₂ O) and gypsum (CaSO ₄ ·2H ₂ O)
3	Calcium oxalate	$\text{Ca}^{2+} \left[\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad / \\ \text{C} - \text{C} \\ / \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right]^{2-}$	Beerstone
4	Barium sulfate	BaSO ₄	Barite
5	Magnesium hydroxide	Mg(OH) ₂	Brucite
	Magnesium oxide	MgO	Periclase
6	Silicates	Me(Si _n O _x) · yH ₂ O	Serpentine, acmite, gyrolite, gehlenite, amorphous silica, quartz, cristobalite, pectolite
7	Aluminium oxide hydroxides	AlO(OH)	Boehmite, gibbsite, diaspore, corundum
8	Aluminosilicates	Al _x Si _y O _z	Analcite, cancrinite, noselite
9	Copper	Cu	Metallic copper, cuprite (Cu ₂ O), tenorite (CuO)
10	Phosphates	Ca ₁₀ (PO ₄) ₆ (OH) ₂	Hydroxyapatite
11	Magnetite or nickel ferrite	NiFe ₂ O ₄	Trevorite

Scaling can even occur in the absence of heating or vaporization, as solubility does not only depend on temperature, but also on pressure. For example, calcium sulfate (CaSO₄) decreases its solubility with decreasing pressure. This can lead to precipitation of scale within reservoir and wells in oil fields, decreasing their productivity with time (Figure 1.4).

Another common salt, barium sulfate, has a differential solubility in solutions with different ionic strength. Similarly, scaling may also occur due to influence of other factors: e.g., liquid flashing, liquid degassing, redox potential changes. Table 2 shows most common scales observed by precipitation out of aqueous solutions.

Mathematics can be used to describe some scaling processes. Advanced equations were developed by different scientists (Bowen, et al., 1978) and (Ruckenstein, et al., 1973) to describe scaling precipitation rates. Simplified approach uses equations below:

$$\text{Transport: } \frac{dm}{dt} = k_t(C_b - C_i) \dots\dots\dots(1)$$

$$\text{Surface crystallization: } \frac{dm}{dt} = k_r(C_i - C_e)^{n1} \dots\dots\dots(2)$$

$$\text{Overall: } \frac{dm}{dt} = k_d(C_b - C_e)^{n2} \dots\dots\dots(3)$$

Where:

m - mass of the material (per unit surface area), kg/m²;

t - time, s;

C_b - concentration of the substance in the bulk of the fluid, kg/m³;

C_i - concentration of the substance at the interface, kg/m³;

C_e - equilibrium concentration of the substance at the conditions of the interface, kg/m³;

n₁, n₂ - order of reaction for the crystallization reaction and the overall deposition process, respectively, dimensionless;

k_t, k_r, k_d - kinetic rate constants for the transport, the surface reaction, and the overall deposition reaction, respectively; with the dimension of m/s (when n₁ and n₂ = 1).

1.1.2 Scale inhibitors

Regarding the paper of British engineer presented at “International Conference on Solving Oilfield Scaling”, the true cost of scale removal from one well can be up to 2.5 million US dollars, and the cost of deferred production can even be higher (Wigg, et al., 1995). So keeping stable and safe hydrocarbon production should be one of the highest priorities in oil and gas industry, as the ultimately most efficient way. Generally scales are prevented from deposition using chemical inhibition, as the most preferred method. Inhibitors can be diluted at producing fluids trough gas lift or topside injection system or being squeezed downhole and used as cost-effective threshold scale inhibitors.

Scale inhibitors are the type of water-soluble chemicals that stops or interferes to nucleation and/or crystal growth of inorganic scales. In addition to nucleation and crystal growth inhibition, some scale inhibitors may perform even scale dispergation as the functioning mechanism. An overview of first chemical scale inhibitors has been published (Gill, 1996). When solution becomes oversaturated and scaling occurs, inhibitors adsorb on crystal surface and diffuse to the active sites. Once inhibitor consumed in the lattice, crystal will grow much slower.

There are different types of chemicals used as scale inhibitors in oil industry. They generally consist of three main types: (a) inorganic phosphates, (b) organic polymers and (c) organophosphorous compounds.

First type of chemicals presents by well-known in oil industry nonpolymeric inhibitors - aminophosphonates. They tend to show good performance at preventing crystal growth by interfering active sites. Unfortunately they are less likely to prevent nucleation if utilized under threshold level.

Second type includes organic polymers which proved to be good nucleation inhibitors and dispersants. If those types of chemicals are applied in combination, increased dosage of polymer will make sure scales stop growing and at the same time increased concentration of aminophosphate will interfere to nucleation. Professor Kelland referred at his monograph "Production Chemicals for oil and gas industry" (Kelland, 2009) to the paper presented by group of researchers at physical chemistry journal at 1978 which stated that only 3 - 5% of the surface of carbonate or sulfate scale crystal need to be covered by some polymeric inhibitors for complete inhibition. This number was higher if small aminophosphonates were used to inhibit barite scale; the necessary coverage for nucleation inhibition in that case was 16%. Some semi empirical mathematical models have been developed for determining scale inhibitor inhibition efficiency, for example, on barium sulfate scale (He, et al., 1996). But this is an empirical approach where coefficients used in the nucleation inhibition model should be determined by laboratory work.

Third type of chemicals consists of organophosphorous compounds which are degradable organic compounds containing carbon-phosphorous bonds. Organic phosphates and phosphonates are typical representatives of this type of scale inhibitors. For the temperatures up to 65-71°C phosphate esters are very effectively inhibit calcium carbonate and calcium sulfate scale deposition. For the fluids with pH higher than 5.5, they also provide good precipitation control of strontium sulfate and barium sulfate scales. In general, organophosphates are soluble in and compatible with high-calcium brines.

Typical chemicals used as scale inhibitors in oil and gas industry are presented at Appendix A. Table was created based on the study of monograph of Norwegian scientist - prof. Malcolm A. Kelland (Kelland, 2009).

1.2 Corrosion control

Corrosion is a big issue for up-, mid- and downstream operations in oil and gas industry. Annual cost of corrosion, according to the paper presented by George F. Hays, general director of “World Corrosion Organization”, is over 3% of the world’s GDP (Hays, 2013). This amount equals to 2.2 trillion of US dollars, which makes this issue really important.

Corrosion is a spontaneous chemical reaction of metal with ambient medium leading to material destruction; mainly it applies to metals, but can also occur at ceramics or polymers materials. Mainly two types of corrosion exist: (a) most common electrochemical, and as name says it is “electro” – electrolyte forming fluid environment, and “chemical” – compound dissolved at electrolyte which reacts with metal, e.g. electrochemical oxidation of metals in reaction with an oxidant such as oxygen; another type of corrosion is (b) chemical or in other words degradable corrosion, where ambient compound – “chemical”, explicitly reacts with metal on its surface.

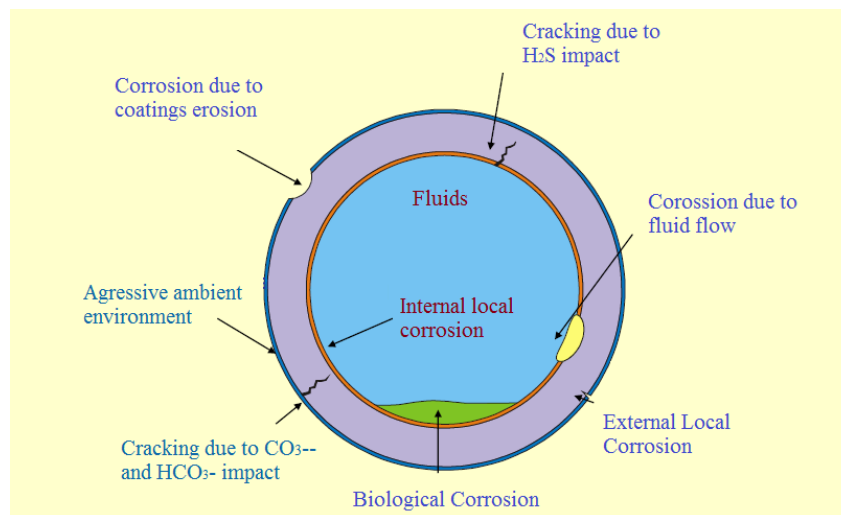


Figure 1.5 - Different types of pipeline corrosion (Tolstikh, 2012)

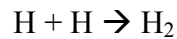
Rusting is a common phenomenon of corrosion. It is a reaction of iron and oxygen in the presence of water or air moisture and is a well-known example of electrochemical corrosion. This type of damage typically produces oxides or salts of the original metal. Due to chemical reaction metal converts to its oxides or hydroxides losing its useful properties such as strength, durability, ductility, structure, appearance and permeability to liquids and gases.

Corrosion can be general or local. First is a basic wastage of metal going over whole surface, second – local corrosion, appears at specific places and can be hard to determine if corroded area is not covered by flaw survey. The consequences of electrochemical corrosion are also embrittlement and cracking, all of which stated above can lead to equipment failure and deferred hydrocarbon production. Embrittlement and cracking of metals are unpredictable processes promoting conditions under which catastrophic failure may occur. As for upstream sector internal and external types of corrosion are the major problem for downhole equipment, production tubing, surface and subsea pipelines, separation units, and storage tanks. Main types of pipeline corrosion summarized at Figure 1.5

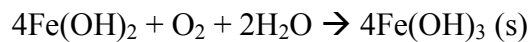
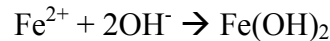
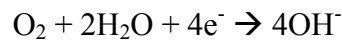
1.2.1 Corrosion theory

Iron in steel can corrode in a presence of water and dissolve species that can form a reaction with iron during oxidizing process. For instance oxygen (O₂), carbon dioxide (CO₂), hydrogen sulfide (H₂S), and natural organic acids in the produced fluids could be the aqueous species that contribute to corrosion. Basically corrosion can be described as an electrochemical redox (reduction and oxidation) process going at the surface of the metal. Both anodic (oxidation) and cathodic (reduction) reactions are localized at the phase boundary (metal-fluid).

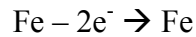
In an acid solution (pH < 4.3), the cathodic reaction is



In neutral or basic solution (pH > 4.3):



At the anode, iron is oxidized for both pH environments:



The basic chemical corrosion processes written above are illustrated at Figure 1.6.

Sulfide species react with diatomic hydrogen which is forming from hydrogen atoms at cathode. Hydrogen atoms will penetrate within metal matrix accelerated by the presence of sulfide components in produced fluids and may lead to sulfide stress cracking. This is another form of corrosion generally occurring later in a field life and is not easily prevented by chemical inhibition.

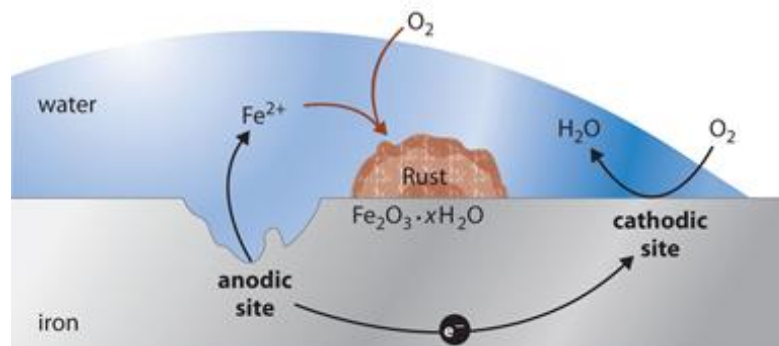


Figure 1.6 - Basic chemical corrosion process (Averill, et al., 2012)

1.2.2 Corrosion control

There are a number of ways of mitigating corrosion presented at the paper written by American researcher (Byars , 1999). Below is a short description of each method summarized in a Table 3.

<u>#</u>	<u>Method</u>	<u>Action and Effect</u>
1	Corrosion resistant alloys (CRAs)	Corrosion resistant. Expensive, but sometimes used downhole if corrosion rates are high.
2	Water removal	Pigging or dehydration. Minimize local corrosion as water removed from water pockets (usually low points).
3	Cathodic protection	Impressed current devices and sacrificial anodes (Al, Zn).
4	Coatings	Paints and plastics. Partly used because of high cost and the possibility of being eroded further opening steel for corrosion.
5	Corrosion inhibitors	Form a protective film on the metal surface. Preventing and inhibiting corrosion.
6	O ₂ and H ₂ S scavengers	Reducing H ₂ S and O ₂ concentration to prevent corrosion.
7	Biocides for preventing MIC	Kills H ₂ S producing bacteria to prevent microbial induced corrosion.
8	pH stabilization	Raise the pH of the produced fluids. Promote formation of hard protective layer as a result of FeCO ₃ deposition.
9	Drag reduction	Utilization of drag-reducing agents (DRA). Reduce flow-induced localized corrosion.

As far as thesis devoted mainly to chemical treatment operations, inhibition chemicals applied during production will be discussed at next section as most utilized corrosion mitigating method in industry.

1.2.3 Corrosion inhibitors

An overview of corrosion inhibitors was presented at the work of Norwegian scientist (Kelland, 2009). He categorized corrosion inhibitors by four groups: (a) passivating (anodic), (b) cathodic, (c) vapor-phase or volatile and (d) film forming.

For protection of anaerobic environments, such as oil, condensate and gas production systems, last group of corrosion inhibitors used. They are likely to form a film on a metal surface preventing of chloride, CO₂ and H₂S corrosion. They can be continuously injected topside at the wellhead or downhole through gas-lift system. Also they can be deployed in batch treatment topside or squeezed downhole.

Passivating inhibitors are not commonly used at oil and gas upstream operations, as they work best for low-salinity brines (e.g. used as freshwater or at condensate water systems). As type D they lead to form a film on the metal surface. This is a nonreactive thin film that prevents access of corrosive species to the metal surface. If underdosed, all inhibitors of this type can even accelerate corrosion and some of them require the presence of oxygen.

Cathodic inhibitors have been utilized as drilling fluids, but as passivating inhibitors, are also not used during hydrocarbon production.

Vapor-phase corrosion inhibitors (VpCI) are chemical compounds that have sufficient vapor pressure to allow vaporization of the molecules under ambient conditions and subsequent gas diffusion and physical adsorption of these molecules on the metal surface. VpCI molecules become polarized in the presence of moisture. Cathode and anode parts of metal will attract different sides of the molecules. For example, dicyclohexylammonium nitrite (DICHAN) will form the ammonium cation and nitrite anion (Figure 1.7).

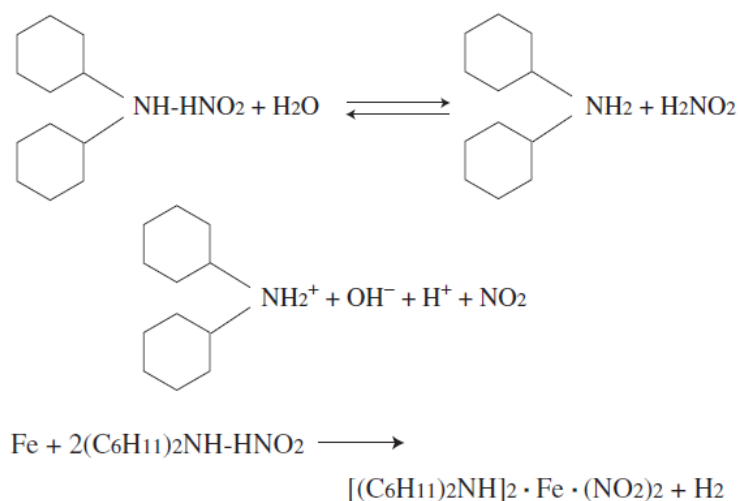


Figure 1.7 - VpCI inhibiting mechanism by (Three Bond Co. Ltd, 1987)

Then formed cation adsorbs to the metal surface and the hydrophobic part of the molecule forms a protective barrier against such species as oxygen, water, H₂S, CO₂, chlorides, and other corrosion accelerators. When the protective barrier is formed on surface, the corrosion cell (cathode-anode) cannot form and corrosion is avoided. The anion will also have corrosion inhibitor capabilities. VpCI has a main advantage of reaching hard-to-access areas between two metal connection sites, e.g. flanges, welded joints or similar systems.

In order to be used, all corrosion inhibitors must be compatible with the protectable metals, comply with the environmental regulations, to be economical for the operations and commercial available. They also should have best desired protective effect and simple way of utilization.

Typical chemicals used as corrosion inhibitors in oil and gas industry are presented at Appendix B. Basic chemicals described, effect and features of each type of corrosion inhibitors stated. Table was created based on study of monograph of Norwegian scientist - prof. Malcolm A. Kelland (Kelland, 2009).

1.3 Biocides

Biocide, also called bactericides or antimicrobials, are the chemical reagents which can deter or render harmless by killing unwanted microorganisms, especially bacteria, or interfering their activity during oil and gas production operations.

Bacteria can be found in different places and forms. Generally they are present in solution (planktonic) form, as dispersed colonies. But as well they can also be found as immobile deposits formed by sessile bacteria plus their waste products. To sustain growth bacteria can utilize a wide variety of nitrogen, phosphorus, and carbon compounds (such as organic acids) presented at producing fluids.

1.3.1 Bacteria impact

Mainly oil and gas industry suffers from the presence of sulfate-reducing bacteria (SRB - *desulfovibrio*), which can be aerobic or anaerobic. Typically they are appearing in all waters handled in oilfield operations. SRB consume sulfate ions (SO_4^{2-}) and convert them to hydrogen sulfide (H_2S) which sour the reservoir. If further produced, H_2S can lead to corrosion and also forming sulfide scales (mainly iron sulfide). Bacteria and their waste products accumulate on wetted surfaces making solid deposits which are called biofilm or biofouling. Pipe with typical biofouling products is presented at the Figure 1.8



Figure 1.8 - Typical pipe with biofouling products

If iron sulfide (FeS) presence or an increase in the water-soluble sulfide concentrations are detected within a flow line, it is a strong indicator for microbial-influence corrosion (MIC). One of the definitions of MIC and its resources was stated at the book “Microbially influenced corrosion of industrial materials” by (Beech, et al., 2000):

"Microbially Influenced Corrosion (MIC) refers to the influence of microorganisms on the kinetics of corrosion processes of metals, caused by microorganisms adhering to the interfaces (usually called "biofilms"). Prerequisites for MIC is the presence of microorganisms. If the corrosion is influenced by their activity, further requirements are: (I) an energy source, (II) a carbon source, (III) an electron donator, (IV) an electron acceptor and (V) water"

To avoid any unwanted process, it is necessary to eliminate its sources. In a case of MIC, bacteria could be killed by biocides or being interfered by biostats. Utilization of those chemicals will prevent the formation of biofilms on the metal surfaces of pipelines and vessels.

Bacteria have the largest ratio of surface area to volume between any life form, meanwhile having a very small size (approximately $1.5 \mu\text{m}^3$). Due to large surface area they can easily sorb diluted metal cations and concentrate them from surrounding fluid. Once metal absorbed they begin to interact with electronegative sites of

microbial molecules. The result of this interaction is a complexation of metal with anions present at ambient fluid. Different types of anions can be found in produced fluids; that is the reason why diverse mineral scales are commonly found in oilfield biofilms. At some oilfields at Middle East iron sulfide was found at biofilms even together with uranium salts (Bird, et al., 2002).

1.3.2 Bacteria control

Kelland M. stated five basic methods to minimize reservoir souring at his monograph (Kelland, 2009):

1. Utilization of biocide chemicals for killing bacteria (SRB);
2. Treatment of bacteria (SRB) with a biostat (metabolic control inhibitor) interfering their growth;
3. By adding nitrate ions nutrients to stimulate formation of nitrate-reducing sulfide-oxidizing bacteria (NR-SOB), which form nitrite control biocide and thereby inhibit SRB growth;
4. Utilization of sulfate-free water or desulfated seawater for water injection operations;
5. Usage of H₂S scavenger.

Ultraviolet (UV) radiation is another bactericidal method that has been investigated and utilized at some oilfield, for instance Ekofisk (Hamouda, 1991). Paper stated that UV method was not killing all SRB, so that was the reason why secondary bactericidal treatment was utilized downstream sterilization column.

First four methods are usually used at water injection systems, while H₂S scavengers are injected downhole or topside into production stream. Biostats and nitrate nutrition treatments can be used simultaneously.

Biocides have been applied at many processes of upstream operations. They were utilized during drilling and fracturing operations, at the inlet and outlet of separation equipment, for the well treatments operations in order to reduce H₂S production and avoid further corrosion and scaling due to biofouling. Most biocides are used for water injection applications for enhanced oil recovery (EOR) from raw seawater environment. SRB will produce H₂S which can cause a significant damage to water injection units by corroding pits and holes in metal pipe walls and equipment.

1.3.3 Chemicals for bacteria control

As stated at previous sections, there are two main types of chemicals for control of bacteria used at oilfield applications:

- Biocides (oxidizing and nonoxidizing);
- Biostats (control “biocides”).

While biocides kill bacteria at sufficient concentrations, biostats just interfere with their metabolism minimizing reservoir or fluid souring. Some combinations of biocides can work synergistically having an advantage over single product, as well as combination of biocides and biostats. Only several biocides are able to reduce population of sessile bacteria at the same dosage as they normally kill planktonic

organisms.

Oxidizing biocides attack microorganism and irreversibly oxidize/hydrolyze protein groups in cell structure, disrupting nutrients from passing across the cell wall. They make the same impact on polysaccharides that bind the microorganisms to the equipment surface. As a result, cell loses normal enzyme activity and then dies. Oxidizing biocides are most efficient between other types of biocides as they kill all strains of SRB, but at the same time they require being utilized at quite high concentrations that can lead to corrosion problems. Main chemicals used as oxidizing biocides were summarized within Table 14 at Appendix C as a brief overview of production chemicals monograph (Kelland, 2009).

Nonoxidizing biocides have another killing mechanism. They alter cell walls permeability impeding biological processes within cell, resulting in cell death. Nonoxidizing are less corrosive than oxidizing biocides, in fact, some of them can even inhibit corrosion. Part of biocides have disadvantage that some SRB may be resistant to their influence. Typical nonoxidizing biocide chemicals used at oil and gas industry, their effect and features are summarized at Table 15 (Appendix C).

Other type of chemicals used at oil and gas industry called biostats. They do not necessarily kill bacteria but create antimicrobial barrier which controls bacteria metabolic processes, interfering with their growth. Biostats bereave SRB an ability to produce adenosine triphosphoric acid (ATP), resulting in disability of cell multiplication and further growth. In some cases that can even cause the death of some microorganisms, however this is not a direct function of biostats. Isothiazolones are one class of biostats, which prevents formation of iron sulfide scale. It maintains a low level of bacteria (SRB) and inhibits their metabolic activity. Main types of biostats and their features are described at Table 16 (Appendix C).

1.4 Emulsion breakers

An emulsion is usually a mixture of two or more immiscible or “unblendable” fluids (Wikipedia, 2013). Emulsions are dispersed colloidal liquids. Droplets of one phase (the dispersed phase) are dispersed in a second phase (the continuous phase) which is schematically shown at Figure 1.9.

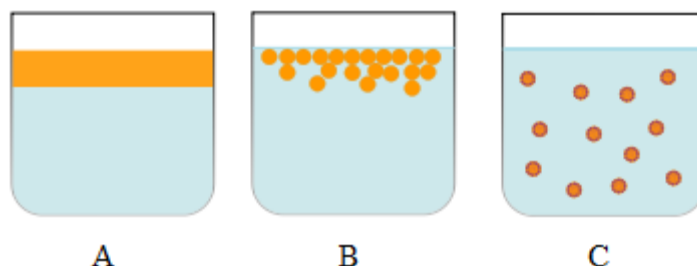


Figure 1.9 - Not yet emulsified immiscible liquids (a); unstabilized emulsion (b); stabilized emulsion (c)

Oil and water are usually produced together during field life. Water cut can significantly increase to the end of production up to 95% (vol.) or higher, but production could be still profitable for some oilfields (Halliburton, 2013).

Produced fluids are almost present as water-in-oil emulsions, when water droplets are stabilized in continuous oil phase. In order for oil to meet transportation requirements water should be separated out. In industry this process is also called demulsification. Maximum water content varies from 0.1 up to 1% depending on separation conditions, transportation and refinery requirements. Also dissolved ion content usually should not exceed 10-25lb/1000bbl to be accepted.

Due to turbulence occurring in the tubing and pipeline, oil and water are actively blended resulting in formed emulsion. This emulsion can be additionally stabilized by solid particles and resins/asphaltenes molecules which are natural surfactants presented in crude oil. Stabilized emulsion is hard-to-split layer formed between oil and water boundary.

Different reactions could occur between oil and water components during production operations. For instance, oil-soluble carboxylic or naphthenic acids can interact with water-soluble cations (Na, Ca, Mg, etc.) forming soaps which can precipitate and stabilize emulsion. Some of production chemicals (e.g. film-forming corrosion inhibitors) are surfactants which can also stabilize emulsions while performing its function. The products of acid stimulation can be back produced after well treatment operations, and as a result stabilize emulsion which therefore needs additional processing with application of demulsifiers and flocculants.

1.4.1 Demulsifying methods

Among different demulsifying methods the most common are:

- Application of emulsion breaker;
- Emulsion heating;
- Electrostatic coalescence;
- Gravity separation;

- Other methods (microwave, sonication, hydrocyclones).

When fluids are heated during processing, wax solids can melt and dissolve at emulsion destabilizing it to some extent. Heating is really common technique for demulsification, but it can play opposite role if carboxylate- or naphthenate-stabilized emulsions are presented at crude oil (Ubbels, et al., 2006). At higher temperatures CO₂ releases out of liquid increasing pH of solution which makes surfactants more polar. Heating provides two effects on demulsification process. When heated, oil becomes less viscous increasing mobility of water droplets to merge and settle under gravity force within oil. Next effect comprises destabilization by reaching phase-inversion temperature. Emulsion will turn from water-in-oil to oil-in-water increasing coalescence of continuous phase.

Usually the final stage of emulsion destabilization process is the application of electrostatic coalescence. Electric current transforms water drops into dipoles by its polarization. Then two polarized drops attract one another and may coalesce (Van den Bosch, 1996).

Gravity separation is a process going on due to different specific weights of components of the mixture, where gravity is the dominant force. It is usually combined with heating and utilization of chemical demulsifiers as the most widely used demulsification technology in oil industry.

A microwave technology uses another type of heat transfer to emulsion: from electromagnetic to thermal energy rather than heat transfer. (Nour, et al., 2010) It has been claimed as a method for treatment of hard separated emulsions (rag layer). “Nonseparated” or “unparted” emulsion is called “slop” or “rag” in oil industry. This is a layer formed between the water-in-oil emulsion and the bulk water. Usually it contains substantial amount of natural and added organic surfactants strongly influencing formation of “slop” oil or rag layer.

Other techniques sometimes used at emulsion breaking processes are: electrostatic demulsification, hydrocyclones and centrifugation. Other methods have also been proposed: thermal flash methods and demulsification by sonication.

Besides all techniques described at this section one of the most important method of breaking emulsions is utilization of demulsifiers. These are the specialty chemicals used for emulsion separation. They are applied at concentration between 5 to 500 ppm depending on water cut. If used in combination with centrifuging, demulsifiers perform good results due to sufficient dispersing and timing, so the water droplets coalesce and phase is separated. Many demulsifiers can also restabilize emulsion if overdosed or over treated.

1.4.2 Emulsion destabilization mechanism and emulsion breakers

For emulsion to be destabilized various system parameters can be changed: density, viscosity, water-cut, aging, control of added or natural emulsifying chemicals (resins, asphaltenes, naphthenic acids, etc.).

Variable parameters, impact processes and their effect are summarized under Table 4.

TABLE 4 - VARIABLE SYSTEM PARAMETERS FOR EMULSION DESTABILIZATION

<u>#</u>	<u>Variable parameter</u>	<u>Process</u>	<u>Effect</u>
1	Viscosity	Heating, adding diluent or other chemicals.	Lowered oil viscosity and hence increased water drop mobility and settlement speed.
2	Density	Heating	Lowered oil and water density. As oil density reduces in higher rate, specific weight difference is increased, leading to rapid water settlement. Not influence much on heavy oil separation process.
3	Water cut	As early as possible emulsion breaking	Low water cuts are harder to resolve, as the water droplets are further apart. Older emulsions tend to be more stable.
4	Emulsifying agents	Chemicals compatibility and interference	Careful selection of chemicals for other purposes may help reduce the use of demulsifiers further downstream.

If emulsion breakers are utilized they first have to be transferred to water-oil interface in order to destabilize emulsion. Interfacial rheology, mass transfer rate, emulsion breaker diffusion rate to the interface and colloid steric effects at the oil-water interface are the factors controlling demulsification process (Tambe, et al., 1995). As better those factors are, more easily destabilization is going on. Basically there are three processes to break emulsion:

1. Flocculation: special chemical (flocculant) adsorbs water molecule on its surface swelling at the same time and forming easily removable flocks;
2. Coalescence: rupturing an emulsified film that has been stabilized water droplets. As film is broken the water droplets merge together and settle down;
3. Solids wetting: moving oil dispersed solids to water phase by wetting.

Many flocculating demulsifiers, coalescing demulsifiers, and wetting agents are used in combination showing synergetic effect.

Majority of water-in-oil demulsifiers are nonionic polymers. They can have complex branched structures with molecular weights variations from 2,000 to 50,000. Cationic or anionic polymers also have found their application as feed stream chemicals or as wetting agents. Most common classes of emulsion breakers have been described at monograph (Kelland, 2009) and are summarized at Table 17 (Appendix D).

1.5 Foam control

Foam is a dispersion of a gas in a liquid (liquid foam) or solid (solid foams) continuous phase. Liquid foaming (Figure 1.10) occurs during crude oil separation processes when gas releases out of solution or during any gas-liquid contact processes used in oil and gas industry.



Figure 1.10 - Liquid foaming

For example in upstream operations foaming occurs at following processes (Dow Corning, 2012):

- Gas-oil separation;
- Drilling mud;
- Gas dehydration;
- Gas scrubbing.

Also at refinery processes it can appear during:

- Crude distillation;
- Vacuum distillation;
- Cracking processes;
- Asphalt processing;
- Delayed cokers;
- Storage tank froth-overs;
- Benzene-toluene-xylene (BTX) extraction.

Foams can be the reason for cavitation and fouling. Some chemicals used for other production issues can also stabilize foams at water systems. High feed rate and gas-to-oil ratio (GOR) also promote foam formation.

Separator foaming can lead to several problems: (a) poor level control that can even lead to platform shutdowns; (b) liquid carryover with gas to downstream scrubbers and compressors which can cause equipment flooding and further failure; (c) gas “carry under” with liquid resulting in increased pump requirements.

Bubbles at foams are stabilized by naturally presented or added surfactants. Natural surfactants are resins, asphaltenes, naphthenic acids, etc. Film-forming corrosion inhibitor is a typical production chemical favoring foam formation. To determine if oil/water system will form foam under experimental/production conditions, few factors have to be evaluated: first - mass transfer along an interface between two fluids due to surface tension gradient (Marangoni effect), second – viscosity which plays a major role.

1.5.1 Defoamers and Antifoams

By utilization of defoamers or antifoams foaming process can be controlled. Antifoam is a chemical that prevents or cast aside foaming. Defoamer act by destroying or destabilizing foam formation that have been already formed (Kelland, 2009).

In oil and gas industry defoamers are also usually called antifoams, maybe because they also act as antifoam and vice versa. These chemicals are usually applied at concentrations of 1-10 ppm for separation processes. Treatment concentration and dosage have to be optimized in order to find optimum because in case of overtreatment these chemicals can even stabilize foams.

Mechanism of foam destabilization by defoamers and antifoams is pretty simple: they displace surfactants from the gas-liquid interface of bubbles and allow the liquid to coalesce and settle, releasing the gas out of the foam. One of the main disadvantages of defoamer and antifoam applications is that these surface active chemicals are highly insoluble in water. That is the reason why they often formulated as a dispersion of tiny droplets, as an emulsion.

Laboratory tests have to be performed in order to evaluate defoamers and antifoams efficiency. Common technique is using graduated measuring cylinders. First, foam is formed in the cylinder, then defoamer is added and time is measured until foam is full destroyed. Same procedure is used for antifoam testing except it is first added to the liquid and then gas is bubbled to form a foam. A time delay in forming a certain amount of foam is measured.

Typically there are two main classes of chemicals used for foaming destabilization in oil and gas industry:

- Silicones and fluorosilicones;
- Polyglycols.

Sometimes they can be used in blends or with hydrophobized silica particles, which have an additional destabilizing effect on foams. Colloid metal oxide particles (fumed silica - SiO_4) consisting of microscopic droplets of amorphous silica have an extremely low bulk density and high surface area. They can also be coated with a defoamer chemical, which both penetrate the surface of foam bubbles, making them coalesce and settle when defoamer spreads between foam formations.

Basic chemicals were highlighted at production chemistry monograph (Kelland, 2009) and are summarized at Table 18 (Appendix E).

1.6 Flocculation

From the chemistry point of view, flocculation is a process wherein particles suspended within continuous phase settle down or adhere to the surface in the form of flocs or flakes (Wikipedia, 2013). These flocs can come out spontaneously or due to addition of specific chemicals. Colloids are not dissolved in liquid phase, but suspended, what is the main difference between precipitation and flocculation.

In the oil industry separated water after demulsification usually contains residual amounts of oil and dispersed solids. The oil is dispersed within water presented in a form of inverse emulsion (oil-in-water). As far as residual oil has an economical value and due to environmental regulations concerning discharges of the water, oil content has to be minimized as much as possible. Discharges standards vary in different regions usually not exceeding 50 ppm (50 mg/l) and can be set as low as 5-10 ppm which is quite hard to achieve. For example, Australian standard is 15 ppm. Solids contained within the water can plug perforation and near-well area if the water is further used for injection purposes. They can also plug filters, raising pressure and damaging equipment which in worst cases can lead to well shutdown.

The oil extraction and solid removal are two main reasons why water should be clarified. There are some methods that are utilized within oil and gas industry. One of them is adding a flocculant, also called as “water clarifier”, “deoiler”, “oil-in-water demulsifier”, “reverse emulsion breaker”, or “polyelectrolyte”. Typical flocculants used at industry were described under monograph by (Kelland, 2009) and are summarized at Table 19 (Appendix F).

Flocculation is chemical process utilized in oil and gas industry in combination with other processing units: filtration, settling, centrifuging, flotation, etc. Flocculants form flocs or flakes by absorption of dispersed oil droplets and solid particles. An example of flocs extracted residual oil is shown at Figure 1.11

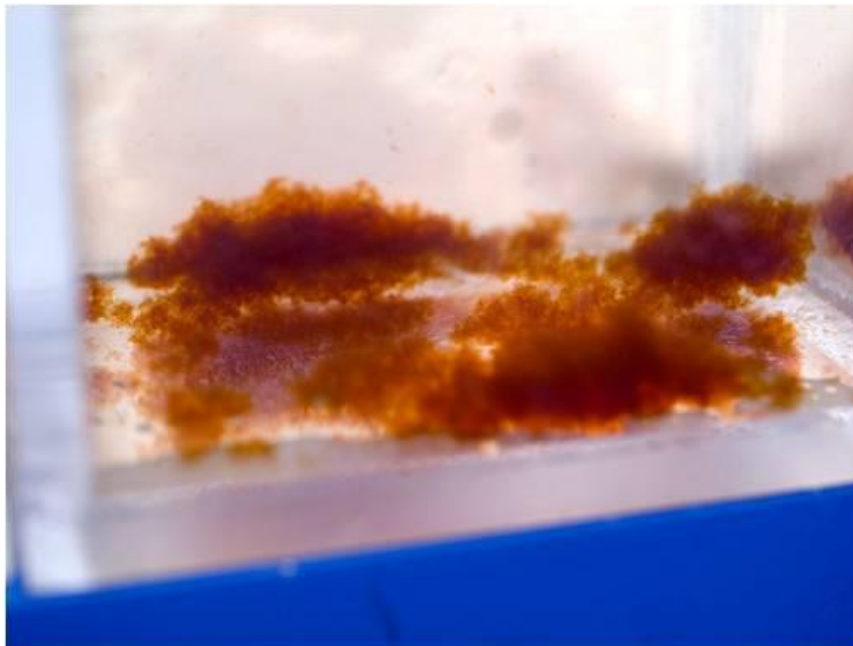


Figure 1.11 - Oil containing flocs

Flocculation product is then separated, oil released and turned back to crude oil flow. Depending on density of final product, flocs can settle down, float on surface or even adhere to the surface inside the equipment. If they are not removed in relatively short period of time, then this might lead to equipment shut down, failure and further cleaning due to buildup and flocs accumulation. Chemicals used for flocculation process can be formulated in a way that flocs will have appropriate size not causing any plugging operational problems.

Besides chemical flocculation there are other technologies that have been developed to remove residual oil and solids from produced and separated water. Brief overview of those techniques is shown at Table 5.

TABLE 5 - WATER PURIFYING PROCESSES		
<u>#</u>	<u>Process</u>	<u>Features & Effect</u>
1	Degassing and flotation	Utilized for water systems with considerable amounts of oil and gas. Flotation unit creates rotation, which forces the lighter components (oil and gas) to inner cylindrical wall. Then oil droplets coalesce and rise to surface where they are removed from the outlet.
2	Macroporous polymer extraction	Hydrocarbon-contaminated water is passed through a column packed with porous polymer beads that contain a specific extraction liquid. The immobilized extraction liquid removes the hydrocarbon components from the process water. Currently in offshore use.
3	Specially designed centrifuges or hydrocyclones	Rotational and forces helps oil droplets to aggregate and float to the surface. Rotational forces are much higher than in first process unit.
4	Oil coalescer, a cyclonic valve and adsorbents for organic materials	Combination of three methods provides better efficiency and deep water purification.

1.6.1 Flocculants

In order to get solid particles and oil droplets to coalesce, chemicals have to be added and mixed. Flocculant should have opposite charge to attract dispersed oil or particles. They can also play a role of “bridge”, causing particles to come together. Bridging mechanism is schematically shown at Figure 1.12.

For this purpose usually utilized large, charged molecules, such as polymers. They can be pre-synthesized or being generated in-situ. As more particles are absorbed by polymer – more charge is neutralized, which shifts polymer geometry from being more open and linear to globular structure, bringing oil and solid particles together. The final structure of polymer makes chemical collapse as a floc.

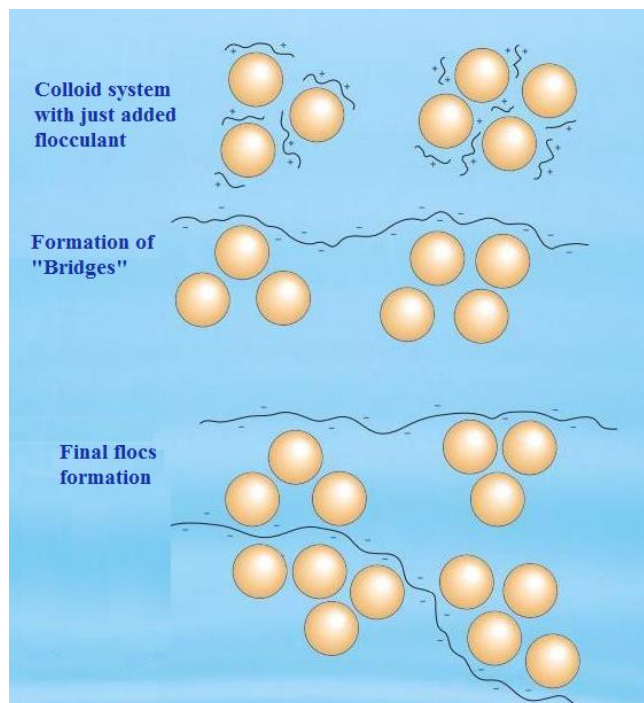


Figure 1.12 - Flocculation mechanism

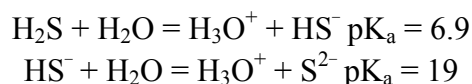
Chemicals used for flocculation contains a large charge on its surface, as this should destabilize dispersion of oil and particles as one of the impact parameter. In general, flocculant purpose is to overcome charge repulsion of imparted anionic surface potential of hydrophobic particle which repels similar anionic surface on the other particle. As more ions are dissolved within water, the charge repulsion becomes weaker. The surface active agents (resins, naphthenic acids, etc.) presented in oil or formed during production (rust, scale, etc.) will dissolve at water phase and stabilize oil-in-water emulsion by surrounding oil droplet and preventing them from agglomeration. That is why flocculation polymers are also used with surfactants.

1.7 H₂S scavengers

For produced gas to meet transportation, processing or sales requirements a concentration of hydrogen sulfide (H₂S) must not exceed few ppm (approximately 4 ppm). It is very toxic, colorless gas with indicative odor of rotten eggs. It is heavier than air very corrosive and explosive. Presence of H₂S during production operations may cause several problems. Being exposed at even low concentration, it can damage health or even lead to death. At higher concentrations it becomes odorless and is really dangerous for human health leading to instant death.

H₂S is quite soluble in water, being a reason for increased corrosion rates. It reacts with steel at equipment surface and pipeline walls leading to formation of pits and cracks or deposition of sulfide scales.

In aqueous systems it dissociates into hydrosulfide and sulfide ions behaving as a weak acid:



H₂S can be generated within hydrocarbon reservoirs by several natural processes.

These are: (a) bacterial sulfate reduction (BSR) by sulfate-reducing bacteria (SRBs); (b) thermal cracking that break apart high molecular weight sulfur-containing compounds, and (c) inorganic thermochemical sulfate reduction (TSR) by hydrocarbons. BSR usually takes place at the temperatures ranging from 0 up to 60-80 °C as SRB cease to metabolize above this temperature. Meanwhile TSR appears to be common in geological formation with temperatures about 100-140 °C (Machel, 2001).

Seawater is rich for sulfate ions (app. 2800 ppm) which are proper nutrients for SRB. If this water is used for injection for EOR, these ions can be converted to H₂S by SRBs and by the TSR process. Reaction products - H₂S often accompanied by smaller amounts of mercaptans (RSH or R₂S), aromatic sulfide species, polysulfides (R-S-S-R), and carbonyl sulfide (COS) will eventually flow to production wells causing lots of production issues (Kelland, 2009). This phenomenon of increase in H₂S concentration has been observed at many places in the world.

Reservoir souring can be mitigated in different ways summarized under Table 6 (Oilfield Wiki, 2012).

TABLE 6 - METHODS TO MITIGATE RESERVOIR SOURING		
<u>#</u>	<u>Process</u>	<u>Features & Effect</u>
1	H ₂ S scavengers	Chemicals added to produced fluid in order to neutralize H ₂ S impact.
2	Biocide treatment	Kills SRB at sufficient concentration to their prevent growth. Biostats can also be used in order to control bacteria metabolism.
3	Nitrate treatment	Prevents SRB population by encouraging nitrate reducing bacteria to use all available donors of electrons.
4	Desulphurization of injection water	Reverse osmosis membrane technology is used to reduce sulfate ions concentration for injection applications.

Not all the sulfate ions can be removed from seawater, as well as not all SRB bacteria can be killed, but enough are removed or killed to significantly reduce reservoir souring as well as sulfate scaling issues. The preferred method for reducing H₂S and mercaptans content from natural gas or oil is using chemicals converting agents – H₂S scavengers. They irreversibly react with H₂S forming reaction products stable at even high temperatures. Different chemical reagents have been used to scavenge H₂S including caustic, peroxides, formaldehyde, nitrites and many types of amines (Baker Hughes, 2011). All chemicals react with H₂S or mercaptans converting them into other sulfur compounds.

To remove small amounts of H₂S and other sulfur components batch treatment can be used. With low gas rate and H₂S concentrations some other batch chemicals can be used: solids or liquid slurries, nitrite, aqueous ClO₂, zinc or iron oxide slurries, formaldehyde/methanol/water, molecular sieves, iron sponge, and other proprietary metal-based processes which have been described by Malcolm Kelland under his work at University of Stavanger (Kelland, 2009). Chemicals were summarized and presented at Table 20 (Appendix G).

For oilfields applications the most economical solution of H₂S removal is installation of regenerative system for treating the sour gas. Absorbent is circulate between absorber, where it selectively reacts with sulfur compounds of produced gas, then saturated fluid is going to desorber, where initial absorbent regenerates and H₂S releases in concentrated form and can be further used at modified Claus process (Fig. 1.14) to form elemental sulfur. This process is known as gas sweetening, which schematically presented at Figure 1.13.

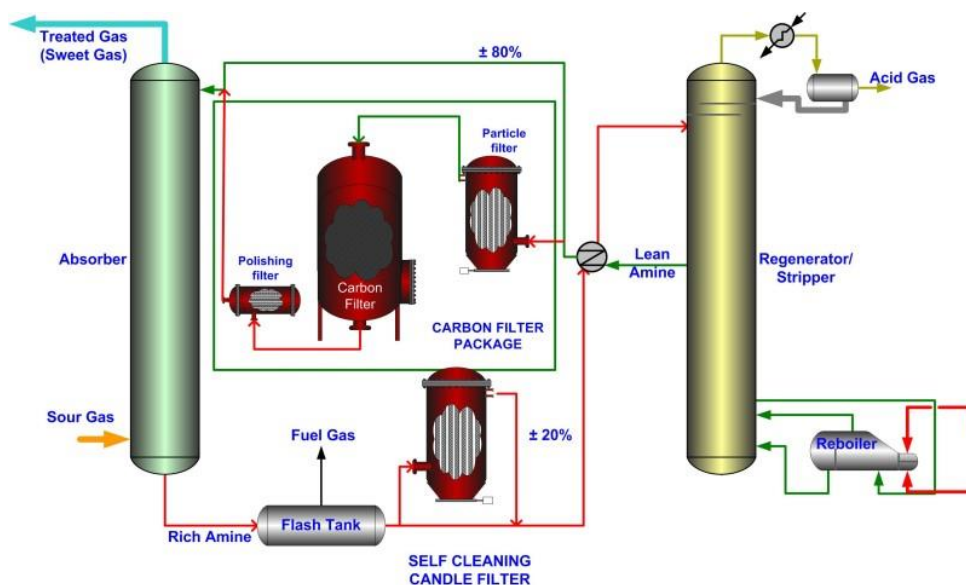


Figure 1.13 - Gas sweetening by (Sulphurnet, 2013)

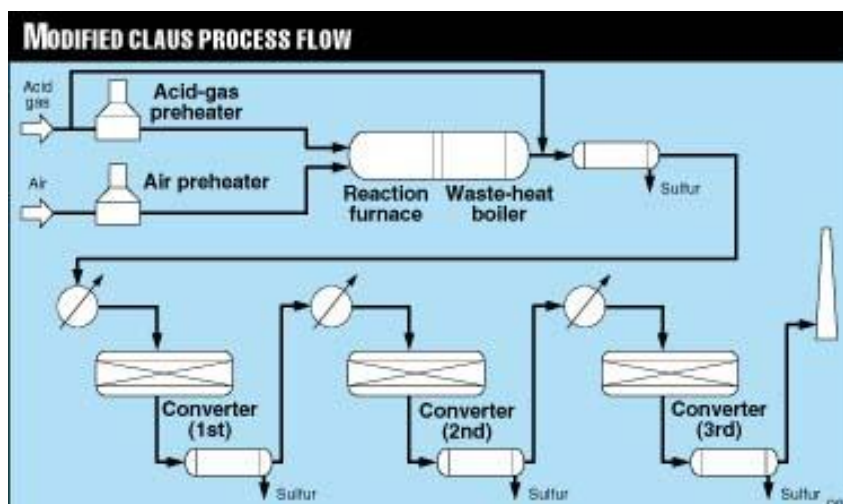


Figure 1.14 - Modified Claus process H₂S conversion to elemental S by (Harruff, et al., 1996)

2 OILFIELD-1 CHEMICAL TREATMENT OPERATIONS

This chapter will mainly focus on chemical treatment operations used for solving production issues at one of the oilfields at Norwegian Continental Shelf. Overview of production streams (3 phase, oil, gas, water) will be discussed further. Chemicals associated with these streams are highlighted for each facility. Chemicals injection systems are shown for one production and one processing facilities.

Due to information policy of operating company all information regarding oilfield data was anonymized. Instead of real, name “Oilfield-1” was used. No references to the data are provided, as far as they point on that particular field. Majority of data of production and chemical systems became available from operating company.

All platform names are replaced with numbers (facility 1, platform 2, etc.) and all wells connected to facilities have their name replaced by two digit number; first number refers to the facility to which well is connected, second number is the well order number (well 1-1, well 1-2, etc.).

2.1 Development and structure of the Oilfield-1

Oilfield-1 is located in the west-southern part of the North Sea. The water depth is about 70 – 75 meters. First hydrocarbon streams were produced direct to the tankers until concrete storage tank was installed. Then Oilfield-1 was developed with many other platforms and facilities expanding connectivity to associated, smaller oil and gas fields. Export pipelines were built to transport oil and gas direct to onshore processing facilities. Nowadays operating company has a big project regarding decommissioning and further disposal of several facilities.

Produced amounts of oil and gas from the Oilfield-1 and associated fields have end up in couple thousand billion NOK (2010) from the beginning of the production. The license partners have invested a bit more than half billion NOK into the field. Recouped net profit was about two hundred billion NOK. Taxes and royalty to the Norwegian state have been amounted to be about thousand billion NOK. Production license will expire by the end of next decade, but operating company and license partners have a plan to extend it till the mid of XXI century.

The Oilfield-1 has quite developed structure. It has 12 facilities (excluding facilities used for associated fields) of which 7 is connected by bridges being comprised under one “Complex”. Most of the facilities are connected by gangways, but some of them are standalone platforms. Oilfield-1 infrastructure is summarized under Table 7.

Actual complex visualization is shown under Figure 2.1. The operative parts of Oilfield-1 consist of the production (F1, F2, F3, F4, and F5), processing (F4 and F6), accommodation (F7, F8 and F12), riser (F9) and injection (F10 and F11) facilities. Some platform has additional dual functions: like drilling (F3 and F5) or processing (F4).

A plan for water injection at oilfield was approved later in a field life. Several plans for development and operations (PDO) were approved by Norwegian government since it was discovered and production started. Accommodation facilities F7 and F8

will be replaced by new living platform very soon according to operator plans. Permanent cables for reservoir seismic acquisition have been installed on the seabed.

TABLE 7 - COMPLEX AND STANDALONE FACILITIES

#	<u>Facility (F)</u> <u>name</u>	<u>Purpose</u>	<u>Connected with</u>
1	F1	Oil producer; wellhead; 23 associated wells	Standalone; Production streams go to F9
2	F2	Oil producer; 24 associated wells	F10 by gangway; Production fluids by pipeline to F4
3	F3	Drilling; oil producer; 23 associated wells	F7 and F8 by gangway; Production fluids mixed with F9 stream
4	F4	Oil producer; wellhead; processing; 30 associated wells	F6 and F12 by gangway; Production fluids mixed with F2 stream; High pressure (HP) well fluids are processed
5	F5	Drilling; oil producer; 50 associated wells	By gangway with F6 and F3; HP well fluids are mixed with F3 & F1 streams and transported to F6; Low pressure (LP) well fluids sent to F6 directly
6	F6	Processing	F4 and 5 by gangway and production pipeline.
7	F7	Accommodation	F3 by gangway
8	F8	Accommodation	F9 and F3 by gangway
9	F9	Riser	F8 by gangway; produced fluids transported to F3
10	F10	Water injection 30 associated wells	F2 by gangway
11	F11	Subsea template for water injection 8 associated wells	Standalone at seabed; Injection water is taken from F10
12	F12	Temporary accommodation	F4 by gangway

Original oilfield recovery technique was pressure depletion with expected recovery factor (RF) of 17%. Due to seabed subsidence it was decided to start water injection to maintain reservoir pressure and to slow down seabed subsidence. Large scale water injection project started after 15 years of development. The actual recovery factor increased a lot, than was expected, because of more efficient water displacement. Chalk compaction provided extra force to drainage of the field. Reservoir compaction led to seabed subsidence by 8-9 meters in the central parts of the oilfield.

Plan for further development is to maintain production from oilfield at a high level through continuous drilling of water injection and production wells from several facilities.

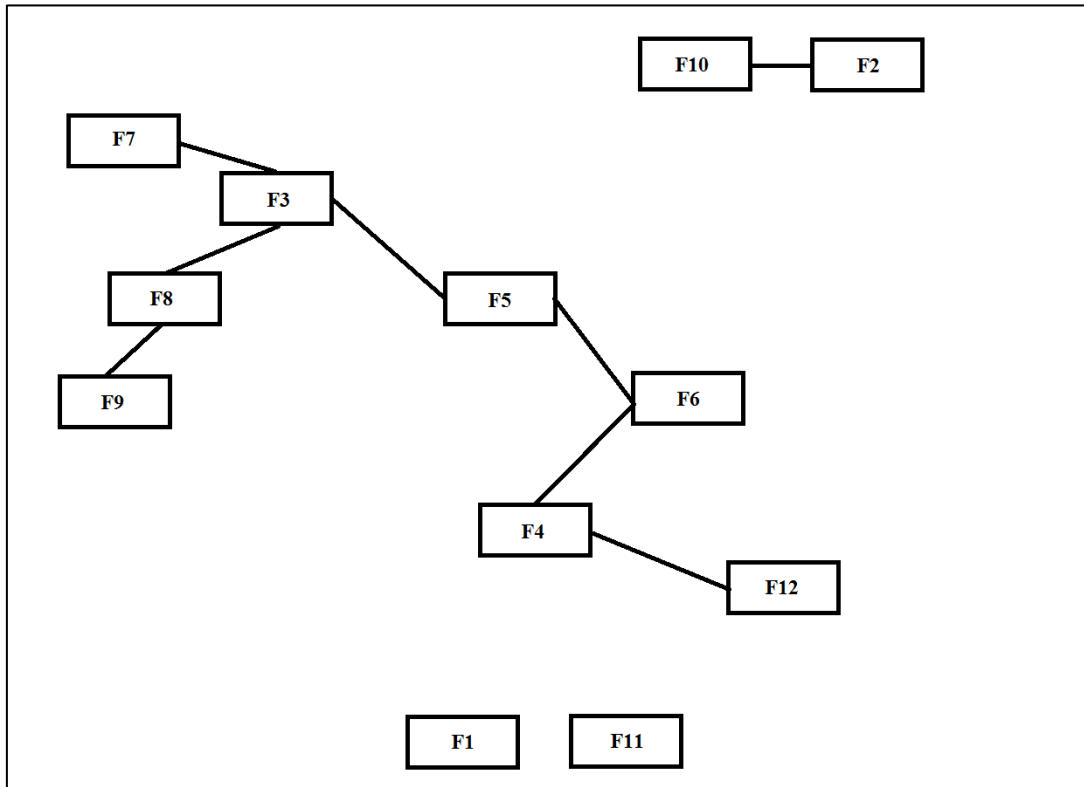


Figure 2.1 – Oilfield-1 infrastructure. Black lines represent gangway connections.

2.2 Oilfield-1 production system

Facilities from the Table 7 are connected together by bridges (gangways), which also could be seen from Figure 2.1. Helicopters or boats are used for transportation between Oilfield-1 Complex and standalone facilities. As might appear at first sight, some platforms are not connected to each other, but it is not a true as far as all standalone facilities are associated with Complex via production pipelines.

Oilfield-1 production streams are routed in a way schematically shown on Figure 2.2. Production fluids from facility F1, located at south part of the field, go to the riser facility F9. Then they combined with F3 three-phase stream and resulted mixture is commingled with F5 HP well fluids. Stream of oil, gas and water is sent to HP separator at F6 for processing and further export transportation. F5 LP well fluids are transported directly to F6.

From the other side fluids from standalone platform F2 (connected by gangway with F10) in the northern part of the oilfield are routed to production/processing platform F4. Produced three-phase flow from F4 HP wells is mixed with F2 stream and further processed at F4 separator. Water is discharged and resulting hydrocarbons are mixed with F4 LP wells three-phase stream and transported to F6 LP separator for processing.

In addition produced oil and gas from associated fields are routed to export pipelines via the processing facility F6. Gas from the oilfield is transported through pipeline to receiving terminal at other country, while oil is sent also via pipeline also to another country for further processing and sales.

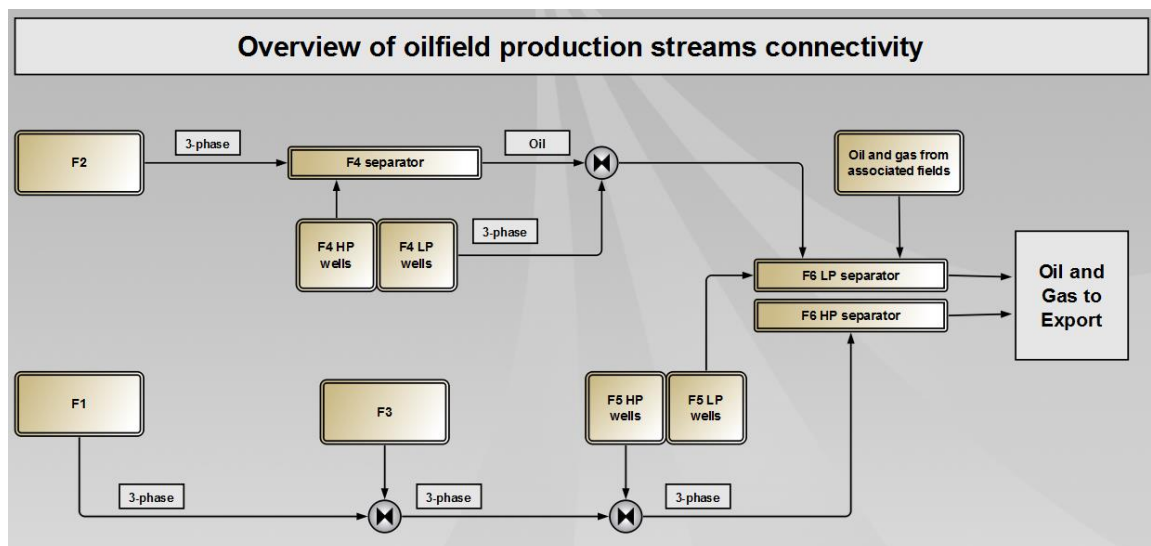


Figure 2.2 - Overview of Oilfield-1 production streams (asset level)

2.3 Production chemicals for treatment operations used at Oilfield-1

This section describes the production chemistry management used at the Oilfield-1. The correct choice of materials and proper facilities design can significantly reduce production issues occurring later in a field life. But lots of problems appear due to unpredictable changes to the production rates, nature of the produced fluids and field conditions. Therefore it is necessary for production chemists to have various chemicals and modern application methods to rectify issues that would not otherwise be fully predicted.

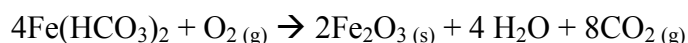
The following chemicals were utilized for treatment during operations at the Oilfield-1: top-side scale inhibitor, gas-lift scale inhibitor, defoamer and antifoam, different types of corrosion inhibitor (for production tubing, manifolds, processing, and export), biocide for process, emulsion breaker, flocculant and H₂S scavenger. Chemical are selected in adherence to OSPAR guidelines for North-East Atlantic and focused on unique produced fluid properties.

Oilfield-1 water has high-salinity content which requires extra care for: (a) predicting mainly scaling as well as other issues, (b) further inhibiting or applying treatment operations, and (c) preventing deposition in the downstream production facilities, for instance at the separator water (oily-water) treatment system. The high content of calcium and iron ions in the produced water provides more difficulties for water treatment.

For example, produced water from one of the associated fields has total dissolved solids (TDS) content of about 200,000 ppm, calcium ion concentration of about 40,000 ppm, and more than 140 ppm iron. Applications of water-dispersible corrosion inhibitor on continuous base, as well as high TDS and solid particles have greatly influenced the stability of emulsion. Sheared oil droplets became highly stable being surrounded by water (continuous phase) at downstream water treatment system. About 44% of the particles had size ranged from 2.5 to 3.2 μm, at the same time 20% of the particles were about 3.2-4 μm. To aid the separation process of the dispersed oil application of flocculant (polyelectrolyte) was required. The high iron concentrations have greatly affected the separation process and led to increased oil discharges to the

sea.

As was found by the production chemist, contribution of iron was caused by two mechanisms. First, ferrous ion (Fe^{2+}) is converted into insoluble iron (Fe^{3+}) oxide (hydrated ferric oxide) in the produced water:



Reaction product (hydrated ferric oxide) has the affinity to adsorb the sludge/rag forming dispersed oil particles. Then this sludge will stick to the equipment walls and desorb oil to the flowing water. Another mechanism comprises effect of iron on scale inhibitor efficiency and perhaps increased concentration of scale particles (BaSO_4 , SrSO_4 , CaSO_4) in the formed sludge. The crystals of the ferrous oxide could become also a crystallization centers for supersaturated fluids promoting further scaling. To treat such aqueous system, a low-pH scale inhibitor blended with an iron sequestering agent was used. This is evident example of the role of produced fluid composition and its conditions on production chemistry choice.

Nowadays there are many chemicals used for production operations at Oilfield-1. They are all distributed between the platforms regarding the processes and production streams going at that particular place. Figure 2.3 shows Oilfield-1 and associated fields facilities, connection of production (oil, water, gas, etc.) and processed streams, as well as the chemicals that have been utilized at particular platform or facility.

Chemicals utilized at Oilfield-1 and associated field production operations are summarized under the Table 8 (supporting chemicals are not included).

TABLE 8 – OILFIELD-1 AND ASSOCIATED FIELD CHEMICALS			
<u>#</u>	<u>Application</u>	<u>Feature</u>	<u>Chemical Name</u>
1	Corrosion inhibitor	Process	CI ₁
2	Corrosion inhibitor	Wellbore	CI ₂
3	Corrosion inhibitor	Batch	CI ₃
4	Corrosion inhibitor	Oil	CI ₄
5	Corrosion inhibitor	Gas	CI ₅
6	Biocide	Process	Biocide 1
7	Biocide	Water injection	Biocide 2
8	Emulsion breaker	Process	EB
9	Antifoam	Process	AF ₁
10	Antifoam	Water injection	AF ₂
11	Flocculant	Process	F ₁
12	Flocculant	Water injection	F ₂
13	Scale inhibitor	Process	TSSI
14	Scale inhibitor	Gas lift	GLSI
15	Oxygen scavenger	Water injection	O ₂ scavenger
16	Hydrogen sulfide scavenger	Process	H ₂ scavenger
17	H ₂ O absorbent	Gas dehydration	MEG/TEG

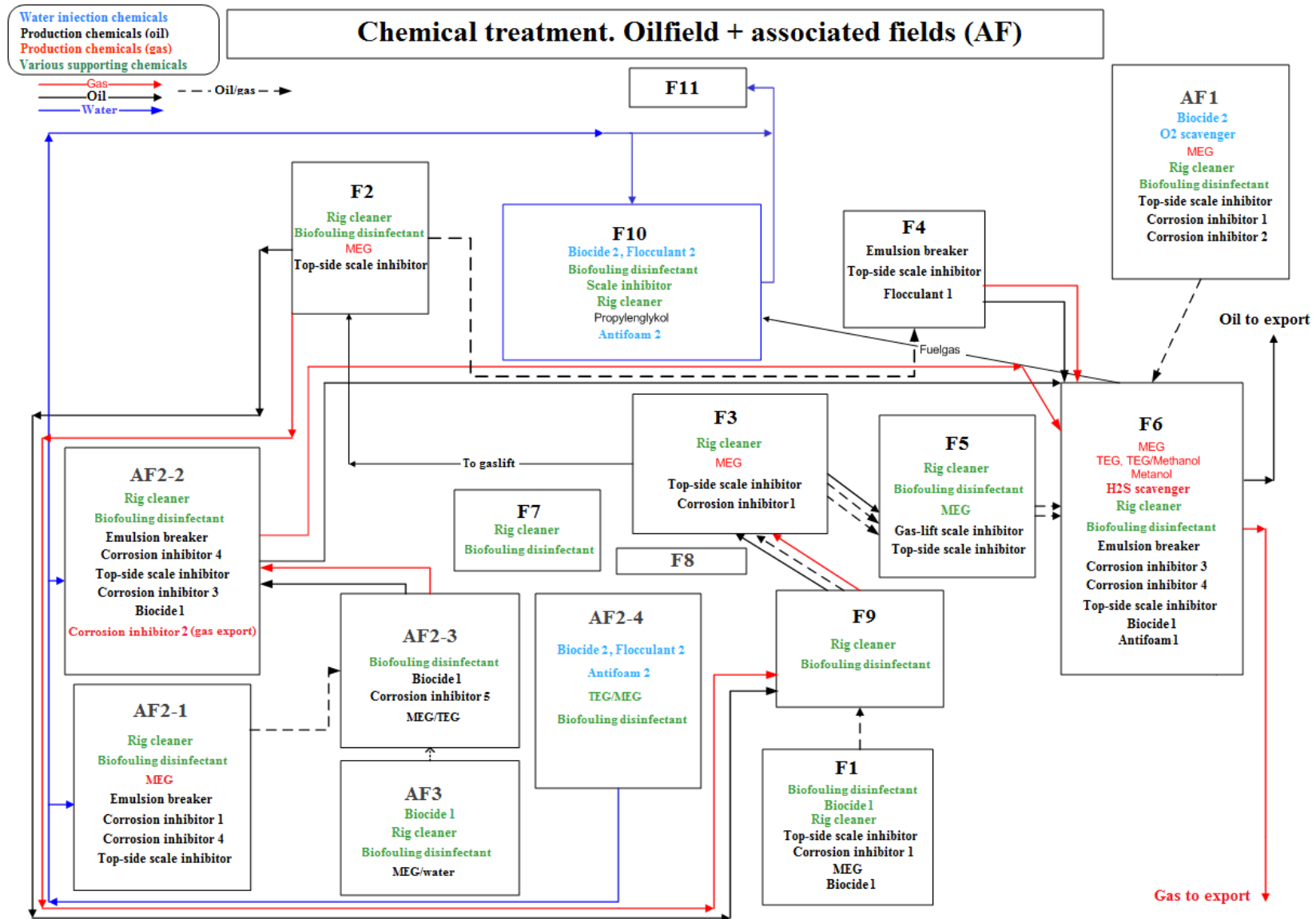


Figure 2.3 – Oilfield-1 and associated field chemicals

As can be observed from the Figure 2.3 almost every facility has to utilize some kind of chemicals. Exceptions are living quarters at F8 and subsea template for water injection F11. To integrate all chemical treatment operations under one management system is quite a complicated task due to the following reasons: (a) lots of production parameters (pressure, temperature, fluid rates, etc.) have to be monitored, (b) samples have to be taken (oil, gas, water) to determine fluid parameters (composition, pH, TDS, etc.), (c) lab experiments performed to determine chemical efficiency and to calculate required chemical dosage. These are time-consuming tasks which have to be performed on a regular basis. Integration of all these tasks under one system will help to reduce working routine and obtain “up-to-date” results.

To create a complicated chemical treatment management system, each issue should be modeled separately and then integrated under one project. At this work, a scale potential monitoring system was created based on synthetic data, which can be replaced by real when it becomes available. As streams coming out of the wells are mixed within manifolds, production system with all mixing points for a particular facility has to be known in order to monitor scale potential variation.

A simplified production streams flow outline and main chemicals utilized at facilities are shown at Figure 2.4. Due to the diversity of the chemicals used at facilities, they are injected with different interims and at different points where production issues might occur. Next sections will discuss chemical treatment systems for production and processing operations going at F5 and F6 respectively.

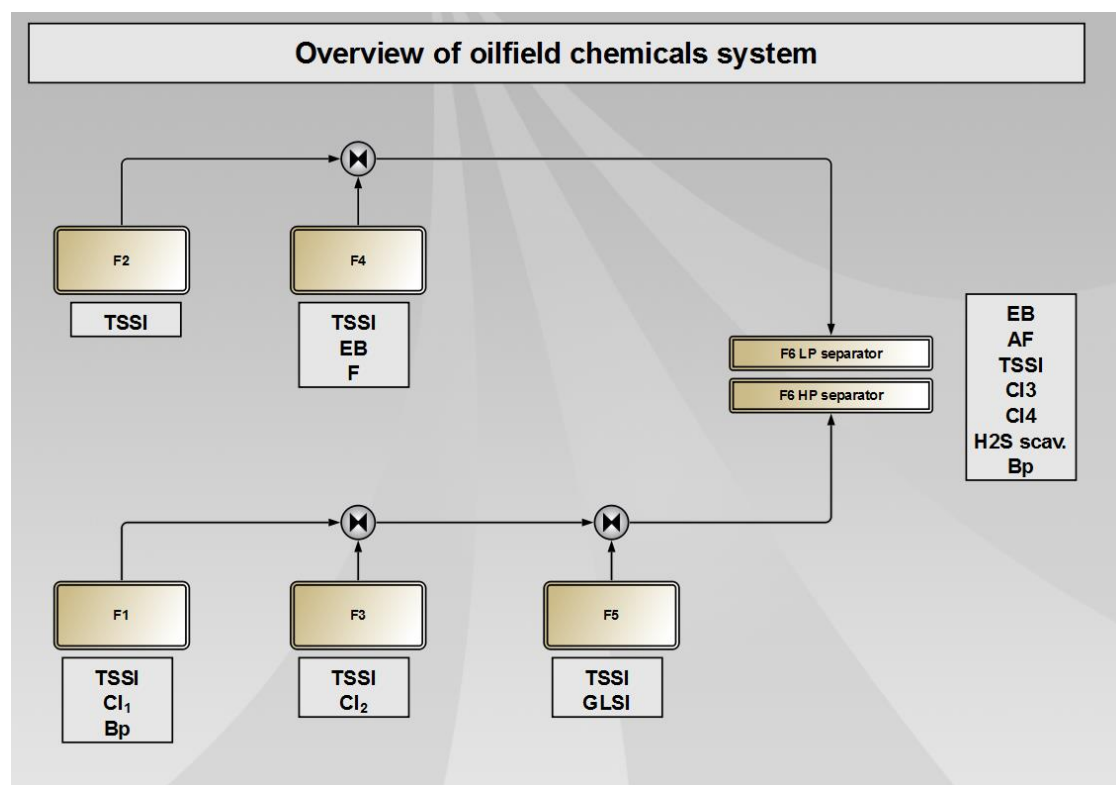


Figure 2.4 – Oilfield-1 production chemicals used at Complex and standalone platforms

2.4 Chemical applications at production platform F5

F5 is a drilling and production facility connected to platforms F3 and F6 by gangways. It is mainly wellhead platform receiving reservoir production before being transferred to processing facility F6. F5 is a compact platform with 50 associated wells, which are planned to replace wells from F1, F2 and F3 in the future. All the wells are producing hydrocarbons and water, except only one which was planned for cuttings injection.

Wells are separated mainly into two groups: north and south. North group contains well 25-50; while the rest belongs to south group. Each group of wells has two production headers connecting the wells: first and second headers are related to south group, while third and fourth to the north group. Those headers have an option to route the wells either to high pressure (HP) or to low pressure (LP) manifolds. All pipelines and manifolds are automated providing opportunity for sustainable production control.

As well fluids are mixed within manifold, water and hydrocarbon amounts will be changed, increasing either water or hydrocarbon volumetric fraction. Water contains dissolved ions, which concentration is also changing with mixing. Due to variation of the production parameters (temperature, pressure, rates), water with dissolved ions may become oversaturated leading to occurrence of unwanted scale precipitation. To prevent scale deposition within wells and headers, each commingled fluid stream formed at mixing point has to be evaluated for scale potential and further decision of scale inhibitors application is determined by production chemists.

Laboratory analysis showed that barium sulfate ($BaSO_4$) was dominating compound within precipitated solids. To inhibit barium scale from deposition few chemicals were used for production operations at F5: top-side scale inhibitor (TSSI) and gas-lift scale inhibitor (GLSI). TSSI chemicals are injected through injection valve located just before the master choke. TSSI system proved to be sustainable treatment operation to prevent scale depositions at manifolds and production header. GLSI are injected downhole to production tubing through gas-lift system. This treatment method was utilized for one well and unfortunately experience showed that it became one of the worst wells associated with F5. To sustain production it was decided to inject inhibitors topside also continuing inhibitor injection through gas-lift system.

Simplified sketch of production system and chemicals injection points is shown at Figure 2.5. Scale inhibitor is injected just right after the X-mass tree before the fluids produced from four groups of wells (North/South – Header 1-2/3-4) are commingled at 8 manifolds. A1-A4 are HP production manifolds, while B1-B4 are LP production manifolds. HP streams are routed to the HP separator located at the processing platform F6, primarily connecting with the three-phase fluid stream coming from F1 and F3. Just before the separator more chemicals are injected for enhanced processing: TSSI, emulsion breaker and antifoam. Same procedure is performed for LP streams, with the difference that they are mixed with three-phase fluids from F2 and F4. Downstream of separators more chemicals are injected during further processing which is discussed at the next section.

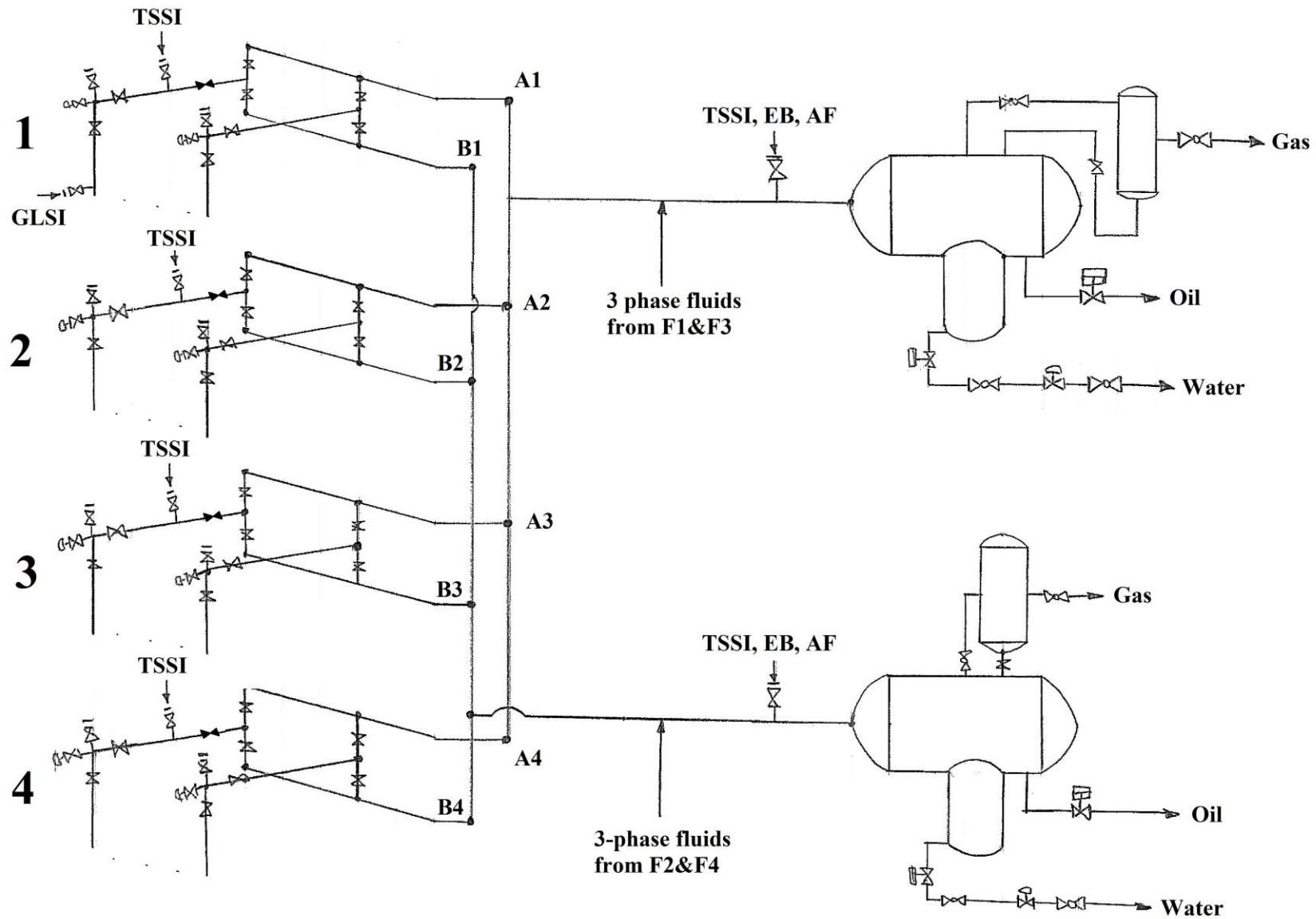


Figure 2.5 - Production system sketch and chemical injection points at F5

2.5 Chemical applications at processing facility F6

F6 is a processing and transportation facility which became operational by the end of last century. It is connected by gangways with F5 and F4. This platform plays an important role as a hub for all production streams coming from the Oilfield-1 and three associated fields. The central control room on the platform controls all processes going on F6 and the connected platforms, as well as the hydrocarbon and water volumes running through the pipelines. F6 platform is the largest energy producer at the Oilfield-1 and associated field area. Energy consumption is adapted to the daily needs and is mainly used for processing, oil transportation, gas export and injection.

After being processed at the platform F6, oil and gas are pressurized and shipped in the export pipelines. Daily processing capacity at F6 reckons up of couple dozen million cubic meters of gas and 300-400 thousand barrels of oil. In addition, oil from associated field number two can 'bypass' directly to the export pipeline. Water treatment facility also located at F6. It cleans produced water from the Oilfield-1 before discharging it to the sea with capacity of 100-200 thousand barrels of water per day.

Outline of F6 processing system and chemicals injection points is shown at Figure 2.6. Tree-phase fluids coming from Oilfield-1 platforms F1, F3 and F5 HP wells are routed to high pressure separator. Before they enter separator three types of chemicals are injected: topside scale inhibitor, emulsion breaker and antifoam.

TSSI can be injected either upstream or downstream of HP separator to prevent deposition of unwanted scale. Demulsifier helps to break emulsion and increase separation efficiency. Antifoam prevents liquid carry out with gas stream to sustain safe and effective production processing. Another type of scale inhibitor is used at HP separator for pipe protection within oil chamber. Processed oil is mixed with the hydrocarbon stream going from LP separator, where the same chemicals are used, except second scale inhibitor.

Water going out of separators is treated with TSSI and sent to water treatment facility for clarification and further discharge to the North Sea. Separated gas from the LP separator is cooled and flashed at the LP scrubber, then compressed to HP separator pressure and mixed its outgoing gas. Combined streams follow the pipeline till they pass the cooler and enter to HP scrubber.

After being flashed, gas is pressurized at HP compressor and H₂S scavenger is injected into the flow line to react and absorb hydrogen sulfide contaminants whose presence can lead to corrosion issues downstream.

If hydrates become an issue due to further cooling at glycol contactor a mixture of methanol and triethylene glycol (MET/TEG) is also injected at the gas stream. For gas to meet transportation requirements and avoid hydrates plugs water presented in vapor phase needs to be removed. Water vapor is absorbed by TEG at glycol contactor until gas reaches required dew point. Then processed gas is routed to export line and rich glycol is sent to TEG regeneration system. Hydrocarbon liquids coming out of contactor scrubber are turned back to LP separator.

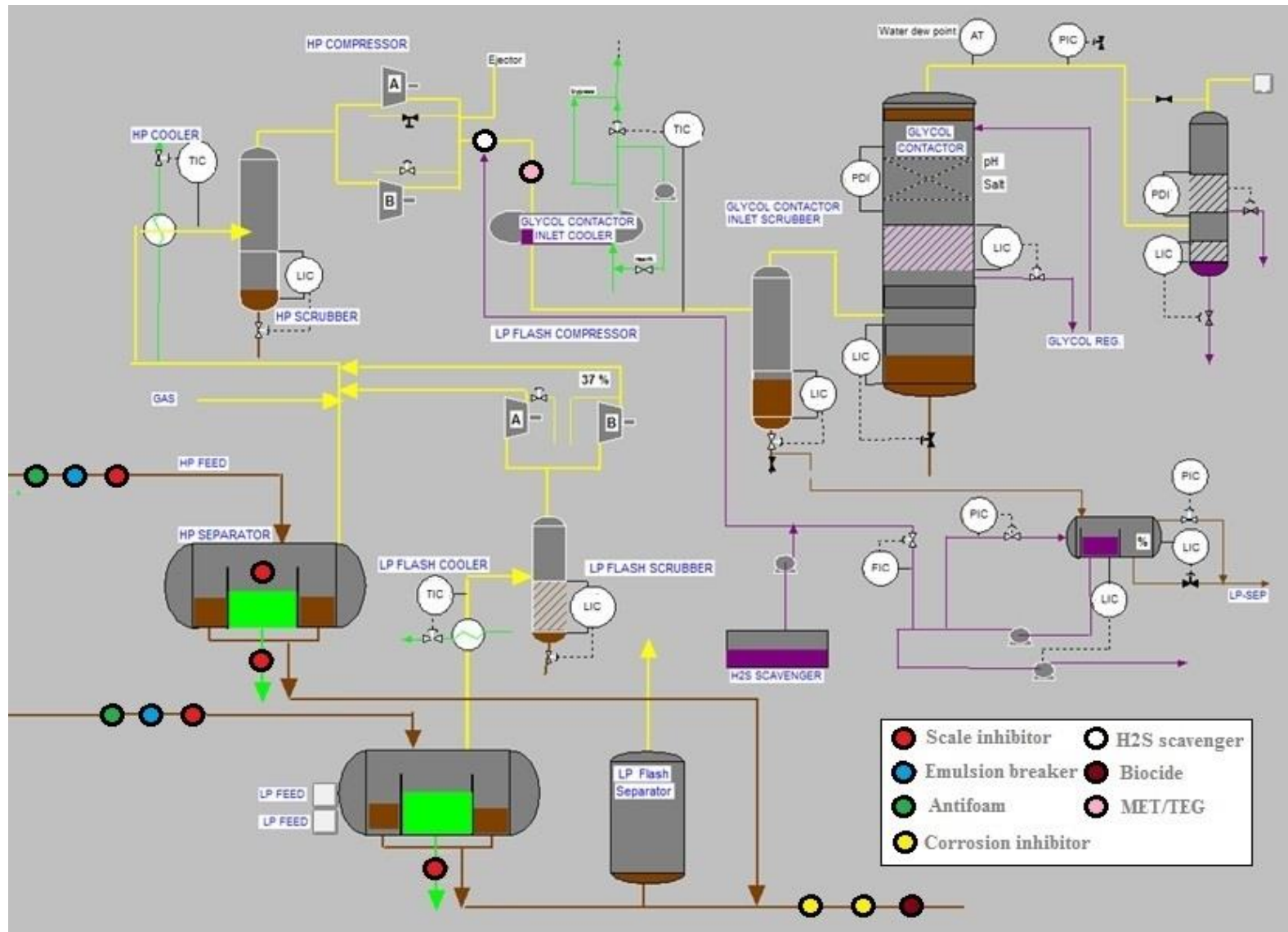


Figure 2.6 - Overview of main chemical applications selected for treatment at F6 processing facility

3 MONITORING AND MANAGEMENT OF SCALING POTENTIAL

Previous chapters stated production issues and chemicals used at actual oilfield to solve occurring problems during production operations. Due to diversity of those issues, to create an integrated chemical treatment system it is needed to adopt each solution “one by one” within the whole project.

To show a concept and procedure to implement treatments applications under one project it was decided to perform this task based on example of particular oilfield – Ekofisk, first oilfield found at Norwegian Sea. It should be noted that Ekofisk information used at further described models is not referring to the real data and any coincidence is accidental.

Ekofisk is an oilfield in the Norwegian sector of the North Sea about located 320 km southwest of Stavanger. It was discovered at 1969 by Phillips Petroleum Company and has been under production over the forty years experiencing lots of production issues. It is still one of the most important fields in the North Sea. In 1971, first oil was produced directly to tankers from four subsea wells. Actual production license expires at 2028, but company plans to extend it until at least 2050.

Different problems occurred during Ekofisk production life. Description of chemicals and treatment methods used during operations at Ekofisk were published by some engineers. To summarize, the following issues occurred and some techniques were utilized to solve those problems:

- Scaling – scale inhibitor for produced fluid and scale inhibitor for injection water (Bakke, et al., 2000) (Hamouda, 1990)
- Corrosion – two corrosion inhibitors for production operations (Bakke, et al., 2000)
- Bacteria control – chlorination (NaClO), shock biocide treatment, UV sterilization (Hamouda, 1991)
- Separation control – emulsion breaker, flocculant, antifoam, polyelectrolyte (Bakke, et al., 2000)

Under the scope of this master work, it was decided to focus on one particular and most widely occurring production issue – scaling. At previous sections was stated the necessity of monitoring production conditions and composition of produced fluids at each mixing point in order to predict occurrence of particular issue. Next sections discuss an approach used at created models to monitor scale potential during production operations in order to provide insight of chemicals demand for production chemists on order to prevent unwanted problems.

3.1 Scale potential monitoring background

To monitor scale potential two computational models of well routing validation were built and integrated within asset integration software called “Pipe-It”. Oddo-Tomson method formed the basis for barium sulfate (BaSO_4) scaling potential (saturation index) calculations and will be discussed at the next section.

First created model is generic model which can be adopted for any oil, gas or gas condensate fields. It has table-view interface and that is why name “Table case” was given to it. Second model is a visualization of table-case model and is more dependent on oilfield infrastructure data, but provides more understanding about on-going chemical treatment processes. It was called “Visual case” model.

In order for models to perform scale monitoring based on Oddo-Tomson method, different data have to be transferred to monitoring application:

- Oilfield infrastructure (facilities and wells);
- Routing of the wells;
- Production data (rates, P, T);
- Ione data.

Last three sources are directly used at Oddo-Tomson calculations, meanwhile first source should be set only once in order to adopt model for particular oilfield. Created models were adopted for the Ekofisk oilfield and required information regarding oilfield infrastructure and associated wells were taken from the open source database available at NPD FactPages (Norwegian Petroleum Directorate, 2013). This source contains information about the petroleum activities going on the Norwegian Continental Shelf (NCS). The information is synchronized with the NPD's databases on a daily basis and is available for everyone.

Routing of the wells is another source needed to define mixing points, because the wells can be connected to different headers and manifolds as have been already shown at previous chapter in the case of production facility F5. Wells routing is decided by production engineers determining connections based on wells, manifolds and headers maximum production capacity load.

Production data is required at Oddo-Tomson calculations to determine amounts of the mixing fluids (for ions concentration recalculation) and the physical conditions (pressure and temperature) at which they are mixed. This data is monitored by controlling devices during production operations and stored at databases together with wells routing.

Last source – ion data provides information about water ionic composition and dissolved scales, which can precipitate as the conditions will be changed or new fluids will be mixed. Production wells are routed to the test separator on the monthly basis and water samples are taken to determine fluid parameters (ion composition, pH, TDS, etc.). Laboratory data is then also stored at databases.

Integration of all these data sources under one system will provide an ability to monitor scaling potential at any time and obtain “up-to-date” results for production chemists.

3.2 Oddo-Tomson method

This section shows an approach invented by American production chemists two decades ago to calculate saturation indices for various scales (Oddo, et al., 1994). It was used in the oil production industry for the most common scales:

- CaCO_3 - calcium carbonate (calcite);
- CaSO_4 - calcium sulfate, usually in the form of gypsum;
- BaSO_4 - barium (barite);
- SrSO_4 - strontium sulfates (celesite).

Ekofisk water has a high sulfate content what makes barium and strontium scale formation is very likely to appear, as those salts have very low solubilities (Hamouda, 1990). Report has shown the dominance of barium scale within deposits and performance tests of some scale inhibitors. For optimal inhibitor utilization it is necessary to predict spots where scaling occurs.

To predict scales, there are some methods available in the oil industry. They are varying from very simple till very advanced methods. Some of prediction methods include (GO-TECH, 2013):

- the Stiff and Davis method to predict the formation of calcium carbonate scale;
- Skillman McDonald Stiff Method to predict the formation of gypsum, barite and celesite scales;
- The Oddo-Tomson method which is a more complex but accurate method of predicting formation of all the common oil field scales.

By calculating saturation indices (SI), Oddo-Tomson method enables to predict formation of various scales. This method is valid in the following ranges: temperature (0 - 200°C or 32 - 392°F), ionic strengths (0 - 4.0) and pressures (1 - 1380 bar or 0 - 20000 psig). Saturation indices can be calculated for the different types of calcium sulfate minerals, including gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$), and anhydrite (CaSO_4). The Oddo-Tomson method has also a possibility to predict the formation of barium and strontium sulfate scales.

To predict scales, method is needed following inputs:

1. Ione data, including calcium, barium, strontium, bicarbonate, carbonate, and sulfate ions;
2. Temperature in °F;
3. Pressure in psia;
4. Mole fraction of CO_2 in the vapor phase or the amount of dissolved carbon dioxide in the water.

If the amount of CO_2 is unknown but accurate pH measurement is available, the method will use pH to calculate the saturation indices. This input was not used for Ekofisk scale monitoring, as system was created for prediction of barium scale formation, which is not needed pH measurement.

The Oddo Tomson method takes pressure as well as temperature and ionic strength into account and for that reason is more accurate than the Stiff Davis method. In addition, it does not need a pH measurement, but calculates the pH based on the

amount of CO₂ gas and bicarbonate in the water. This provides a better accuracy for SI calculation of a water sample, because pH measurements decline in accuracy very quickly after the sample is taken out of its natural environment (GO-TECH, 2013).

Barium sulfate saturation index is calculated based on scale saturation ratio, F_s , defined as a ratio of the ion activity product $[Ba][SO_4]$ to the solubility product (K_{sp}):

$$F_s = \frac{[Ba][SO_4]}{K_{sp}} \dots\dots\dots(3.1)$$

Activity is defined as the product of the activity coefficients and the concentrations of barium and sulfates ions. Ions activity coefficients are the function of temperature, pressure, and ionic strength (I) of solution. The ionic strength is a measure of the concentration of the dissociated ions dissolved in water also called as “total dissolved solids” (TDS). Total concentration of dissolved ions will affect important properties such as the dissociation or the solubility of different salts. One of the main characteristics of a solution with dissolved ions is the ionic strength, which can be determined by following equation:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \dots\dots\dots(3.2)$$

Where c_i is the molar concentration of ion (mole/l);

z_i – charge number of that particular ion.

The solubility product (K_{st}) is a function of temperature, pressure, and ionic strength and was empirically correlated by Oddo and Tomson, represented as a logarithmic expression $-\log K_{st}$ at equation 3.3.

$$pK_{st} = 1.86 + 4,5 \times 10^{-3}T - 1.2 \times 10^{-6}T^2 + 10.7 \times 10^{-5}P - 2.38\sqrt{I} + 0.58I - 1.3 \times 10^{-3}\sqrt{IT} \dots\dots\dots(3.3)$$

The resulting conditional solubility product term pK_{st} is then used in the predictive equations.

Saturation index - SI can then be expressed as the log of the F_s :

$$SI = \log(F_s) = \log \frac{[Ba][SO_4]}{K_{sp}} \dots\dots\dots(3.4)$$

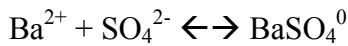
Or rewritten by,

$$SI = \log[Ba][SO_4] + pK_{st} \dots\dots\dots(3.5)$$

When SI equals zero, the solution is at equilibrium with the solid scale; negative values of SI meaning nonscaling conditions of the solution with respect to the particular scale; if saturation index is greater than zero, it indicates a supersaturated or scaling condition.

Barium and sulfate ions can pair and form a complex, resulting in free metal and free sulfate complexation. The extent of reaction depends on the solution parameters (temperature, pressure, ionic strength) and total concentrations of the barium and sulfate ions.

Complex formation between barium and sulfate is described by following reaction:



Where BaSO_4^0 is the neutral ion pair, referring as a complex in solution, but should not be confused with precipitated solid. The stability constant, K_{st} defining the ratio of paired ions to the free metal and sulfate product is given by equation 3.6.

$$K_{st} = \frac{[\text{BaSO}_4^0]}{[\text{Ba}^{2+}][\text{SO}_4^{2-}]} \dots\dots\dots(3.6)$$

The mass-balance equations for the total dissolved calcium, magnesium, strontium, barium, and sulfate ions are stated below. Total molar concentration of sulfate anion in paired and free condition is:

$$C_{SO_4} = [\text{BaSO}_4^0] + [\text{CaSO}_4^0] + [\text{MgSO}_4^0] + [\text{SrSO}_4^0] + [\text{SO}_4^{2-}] \dots\dots\dots(3.7)$$

Total molar concentration of metal species presented in solution can be calculated by equations 3.8-3.11:

$$C_{Ba} = [\text{Ba}^{2+}] + [\text{BaSO}_4^0] \dots\dots\dots(3.8)$$

$$C_{Ca} = [\text{Ca}^{2+}] + [\text{CaSO}_4^0] \dots\dots\dots(3.9)$$

$$C_{Mg} = [\text{Mg}^{2+}] + [\text{MgSO}_4^0] \dots\dots\dots(3.10)$$

$$C_{Sr} = [\text{Sr}^{2+}] + [\text{SrSO}_4^0] \dots\dots\dots(3.11)$$

To solve equations 3.6-3.11 authors made an assumption that stability constants for all four metal/sulfate complexes are nearly equal at room temperature, which greatly simplified the calculation procedure. Those equations were solved as quadratic equations for the free metal and sulfate concentrations in solution, resulting in equations 3.12-3.13.

Free metal concentration can be calculated by:

$$Ba^{2+} = \frac{C_{Ba}}{1 + K_{st}[\text{SO}_4^{2-}]} \dots\dots\dots(3.12)$$

Free sulfate calculations:

$$\text{SO}_4^{2-} = \frac{-1 \{ 1 + K_{st}(C_M - C_{SO_4}) \} + \sqrt{[1 + K_{st}(C_M - C_{SO_4})]^2 + 4K_{st}C_{SO_4}}}{2K_{st}} \dots\dots\dots(3.13)$$

When free ion concentrations are known, it is possible to calculate the saturation indices, based on empirical equation derived by least-square-curve fit of pK_{st} to actual equilibrium solubility data:

$$SI_{BaSO_4} = \log_{10} \{ [\text{Ba}^{2+}][\text{SO}_4^{2-}] \} + 10.03 - 4.8 \times 10^{-3}T + 11.4 \times 10^{-6}T^2 - 4.8 \times 10^{-5}P - 2.62\sqrt{I} + 0.89I - 2.0 \times 10^{-3}\sqrt{IT} \dots\dots\dots (3.14)$$

Saturation indices calculation procedure shown above formed a basis for scale potential monitoring models.

3.3 Integrated scale potential monitoring system

Scale monitoring system was created using the integrative software called Pipe-It. As many fluid streams have to be evaluated for scaling potential at different mixing points, it is needed to bring them together under one application. Pipe-It can do that also allowing graphically and computationally to integrate different models and additionally to optimize petroleum assets operations. Visualization capability with an intuitive graphical layout design provides a clear vision of the project organization in a multi-level architecture, similarly as from top-level management point of view (Petrostreamz, 2013).

Pipe-It philosophy states that user, in order to model real process in oil and gas industry, has to *pipe it* streams computationally just as it is piped physically. Pipe-It represents a workflow in a same way it exists in reality. User can launch any software on any operating system within Pipe-It. It chains applications together, automatically knowing the most-efficient and consistent launching sequence of all applications.

The basic principle behind Pipe-It is really simple. It sends information from a resource to the process, where this information is processed. Then process transfer results into another resource which in turn might be another input for another process forming a computational chain of processes. By using graphical user interface (GUI), it is simply possible to visualize the connections of the project. Computational chain can represent physical flow of hydrocarbon/water fluids in a producing field at different levels: fluid flow from reservoir to the well, from well by the pipeline to the separator, from separator to the market. This process can be easily seen from Figure 3.2

Pipe-It uses three primary elements (building blocks) - resource, process, and connectors. The Resource represents a file on a disk which is connected to the process. Each software application is called Process which also connects input and output resources. User can chain resources and processes with element called Connector (a line with directional arrowhead). Basic Pipe-It elements are presented at Figure 3.1.

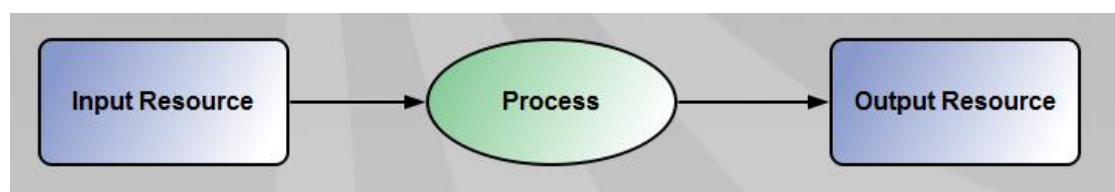


Figure 3.1 - Pipe-It main elements

A fourth and the last key element is called Composite. It is simply a collection of the primary elements and other sub-composites. Composite allows user to build multi-level structure of the project and to decide which level of the project must be displayed according to the objective.

Another great Pipe-It feature is that by using the composites only some parts of the project could be executed, instead of running the whole project. This provides an opportunity to create a project step by step keeping track on the integrity of each element of the project.

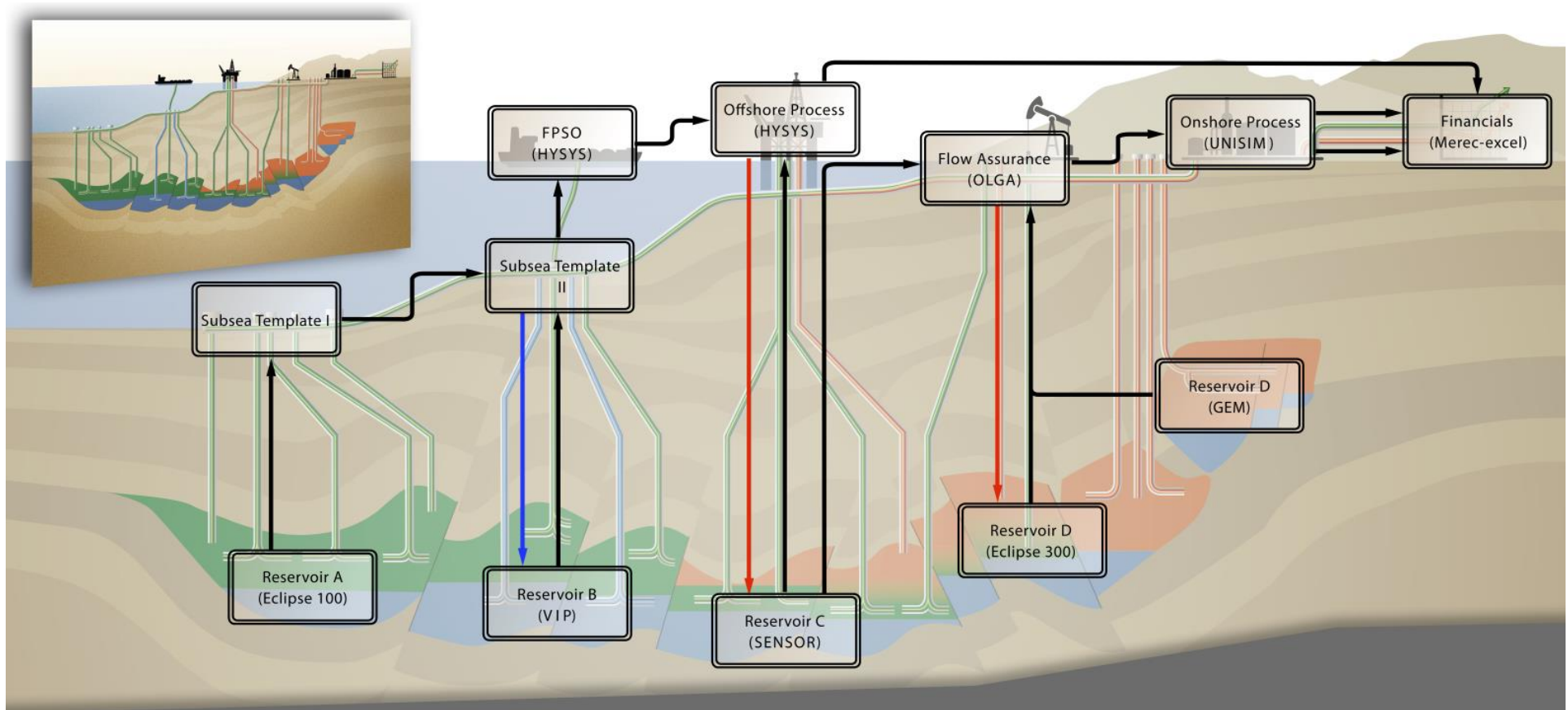


Figure 3.2 - Pipe-It working “philosophy” outline

Chemical treatment management system can be created using Pipe-It, as it allows to chain any software and data files. To launch those applications they have to be executed under the command-line mode (CMD) or with the help of software framework such as Component Object Model (COM) or ActiveX. Unfortunately modern chemical treatment software is not fully capable to be executed under CMD mode, as they are mainly tools for processing and interpreting the laboratory results. Any way as they will be developed it would be possible to integrate them under the Pipe-It project.

Under the scope of this work, it was decided to create a monitoring system for widely occurring production issue – scaling, as it is important in order to prevent scaling, to monitor production conditions and composition of produced fluids at each mixing point.

Pipe-It “table case” model created for particular production facility Ekofisk-X consists of 366 elements, from which 133 are processes, 193 are resources and 40 are composites. “Visual case” model is bigger than previous model due to visualization of oilfield infrastructure. It includes 134 processes, 483 resources and 122 composites.

Before looking at the models organization structure and the information flow, it is important to highlight processes (software) which have been used to create monitoring system.

3.4 Software implemented within Pipe-It models

3.4.1. Streamz

Streamz is a Pipe-It built-in engine. It is a generic program providing underlying technology for streams manipulation - lumping, splitting, translation, etc. and conversion from one to another characterization with really efficient algorithms able to handle unlimited numbers of streams.

It describes stream components and their properties such as molecular weight, critical temperature or pressure, acentric factor and other specific properties. Streamz is driven by a driver file (input) and command-line invoked executable that is part of Pipe-It. Streamz flow is presented at Figure 3.3. Driver file is comprised of streams characterizations with their properties and establish conversions among them.

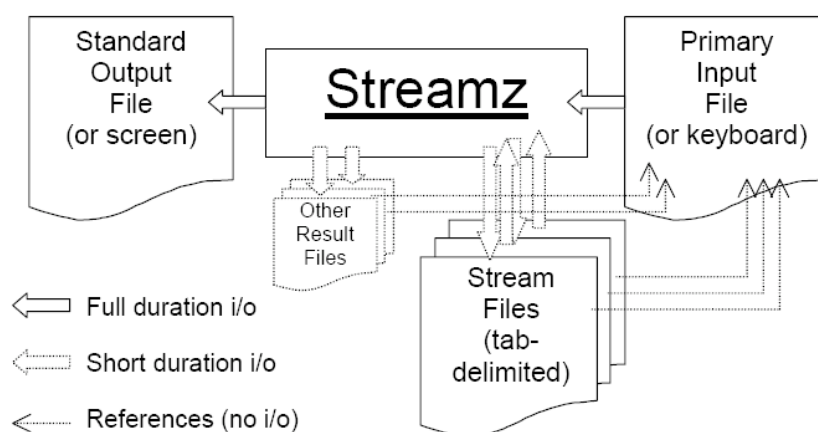


Figure 3.3 - Streamz flow and input/output files

The current version of Pipe-It can launch Streamz with pre-generated driver files in the same way it launches any other command-line program, so there is no need for user to be familiar with the Streamz syntax. The Streamz primitives Copier, Tabulator and some built-in application such as txt2str are available at Pipe-It interface.

Copier is a Streamz component used within scale monitoring models to split the streams into two or greater number of streams. As shown at Figures 3.4-3.5 user has to specify Stream Filter in order to choose specific stream from the input file. In example below fluids described at Streamz file “Header 1 South” are separated by Copier into HP wells stream and LP wells stream.

There are more features available within Copier, such as normalizing the component amounts, multiplying any stream quantities by some number, establishing conversions and obtaining Streamz driver codes.

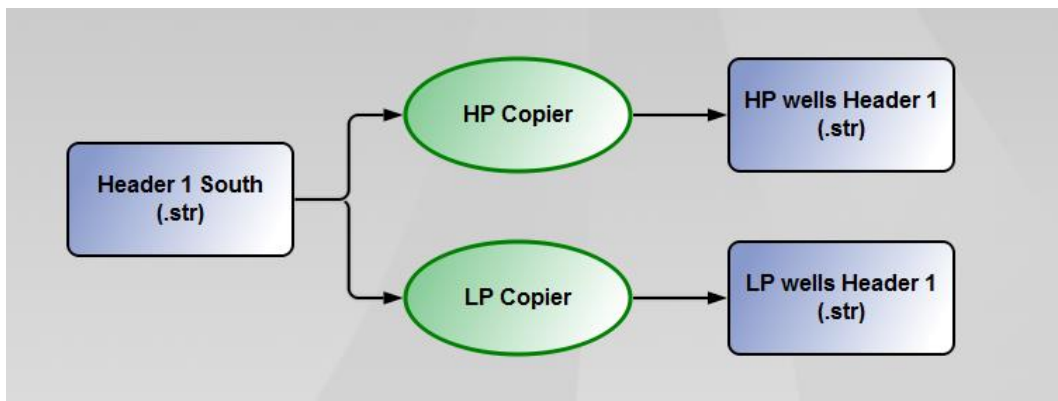


Figure 3.4 - Splitting streams within Pipe-It using Copier

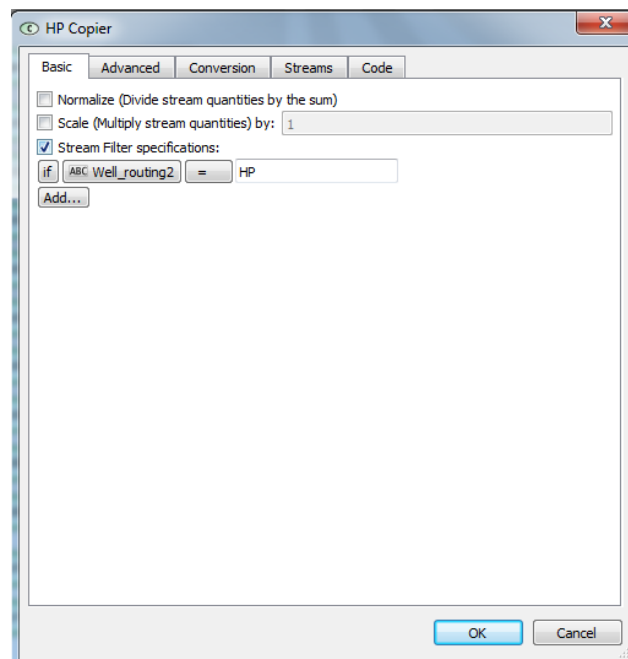


Figure 3.5 - Copier interface

Another Streamz component is called *Tabulator*. It allows user to aggregate or lump streams together. At example shown at Figures 3.6-3.7, well fluids are tabulated together in one header stream. It can aggregate streams based on specific variables, such as pressure, temperature or any other variable. If user needs only to combine streams based on one variable, other parameters can be just displayed. As well as Copier, it can normalize, scale and also filter streams.

There are more features available within Tabulator: at advanced menu item it is possible to define streams gathering order; also as Copier conversions could be defined and Streamz driver codes obtained.

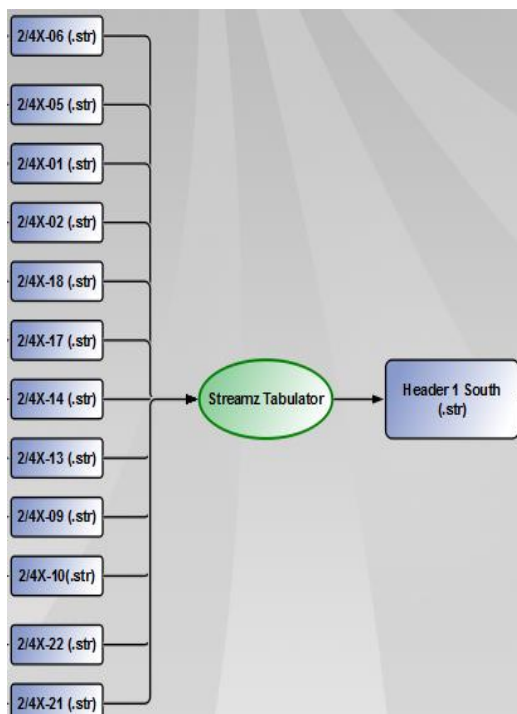


Figure 3.6 - Aggregating streams using Tabulator



Figure 3.7 - Tabulator interface

Txt2str is a Pipe-It utility was used within models to convert files from text format into Streamz internal format files with .str extension. They have specific structure and organization which has to be set by user. *Txt2str* utility mainly copying data from text files filling Streamz files in correct way, so user do not have to create it manually. Then .str can be used at different processes, for instance such as described above.

3.4.2. Linkz and MapLinkz

Linkz is a built-in feature within Pipe-It, providing an intuitive GUI to access input and output information located in Resources. User can “link” to the different types of information such as numbers, text, vectors, or matrices. Linkz can access any data located in the text files, Excel sheets or COM memory (using applications providing access to the COM data structure) (Petrostreamz, 2013).

To locate values inside a resource file, Linkz file viewer should be used (Figure 3.8). User specified Linkz values are highlighted in green. In case below header pressure is specified at the text file. To locate selected value inside the file, Linkz will look for “hooks” or “anchors” tokens (keywords), which have to be defined by user. The link cannot be defined without relatively surrounding tokens.

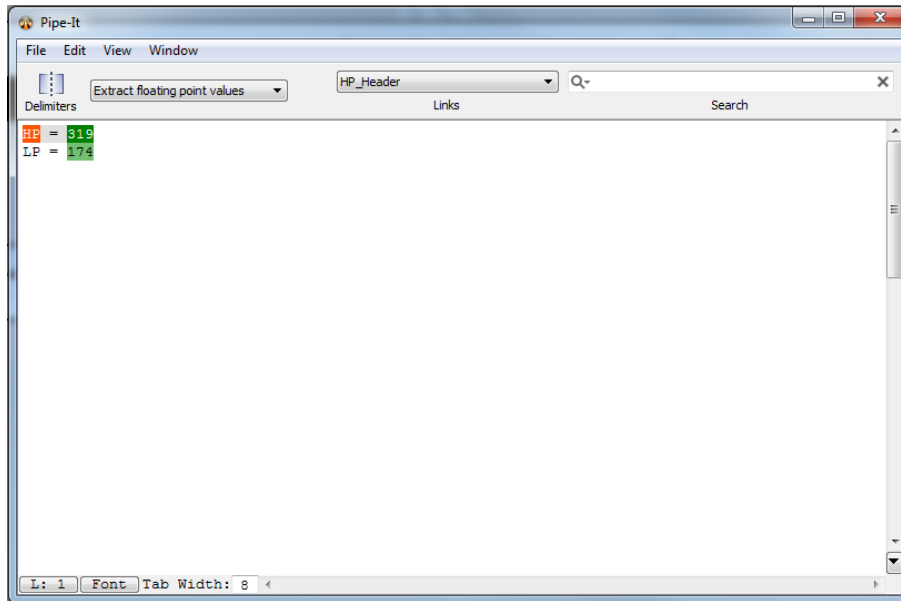


Figure 3.8 - Linkz viewer interface

To choose a linking value user can double click on any number or other information located at file invoking Edit Link window, where all link information can be defined by user such as: link name, type of link (value row, line or matrix), current value of the displayed variable and “hooking” keywords.

3.4.3. Strexzel

Another Pipe-It built-in application is called Strexzel. It has a similarity with actual Excel software application, but only used for reading, manipulating and writing stream files. It can run in a GUI mode where the user can view streams. Simple example of Streamz file opened at Strexzel and showing saturation indices for different wells is presented at Figure 3.9.

	Well_Number	IS_BaSO4
1	25	0
2	26	0.464108
3	27	0.464108
4	28	0.464108
5	29	1.22605
6	30	1.22605
7	31	1.22605
8	32	1.14355
9	33	1.14355
10	34	1.65324
11	35	1.65324
12	36	1.65324
13	37	1.65324
14	38	1.65324

Figure 3.9 - Strexzel interface

To manipulate the streams macro commands can be used (Petrostreamz AS, 2013). Macros are set of commands for stream manipulations which can be saved to disk. When Pipe-It will run the project, it will be executed in console mode. Strexzel will use a macro file commands for the input Streamz file, and create a new processed Streamz file as output. If Strexzel is launched without any command line specifications, it will be just open in GUI mode.

3.4.4. Plotz

Plotting is another Pipe-It feature. This application allows creating plots directly from Streamz files. User has to specify axes with variable or component values. Then plot will be automatically generated allowing saving it on the disk as .plot file. Figure 3.10 shows results of plotted file from previous section.

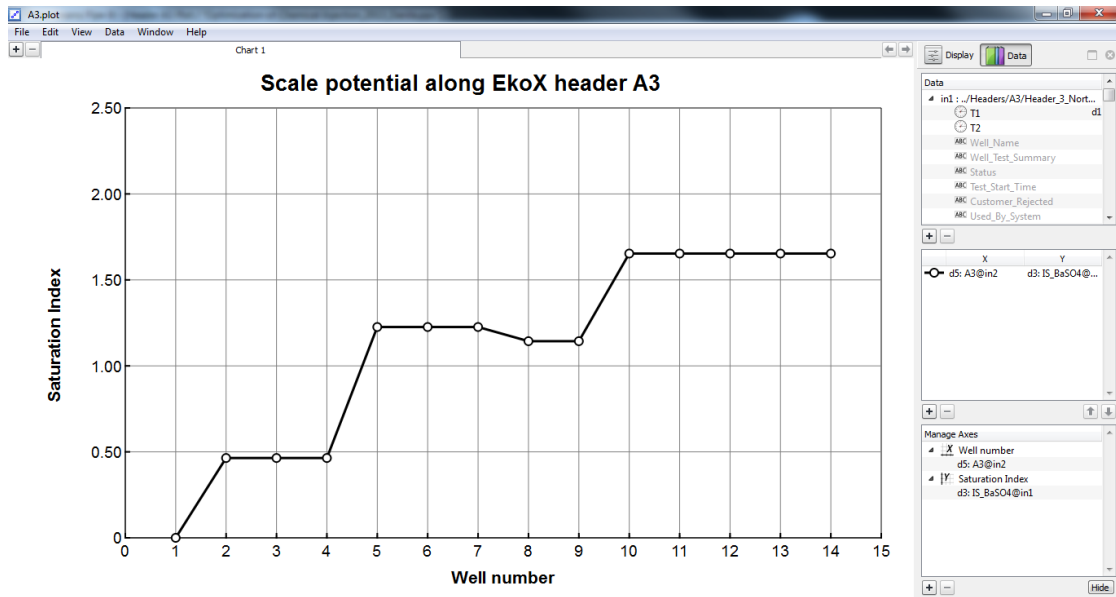


Figure 3.10 - Plotting streamz files within Pipe-It

After being saved, this file can be executed in command-line mode, as shown at Figure 3.11. Input .str and .plot files have to be specified at command-line argument line and format of output file defined. Various formatting types such as Bitmap or JPG as well as PDF can be assigned for output files. This utility was used to generate scale potential plots for monitoring scaling potential development at production headers.

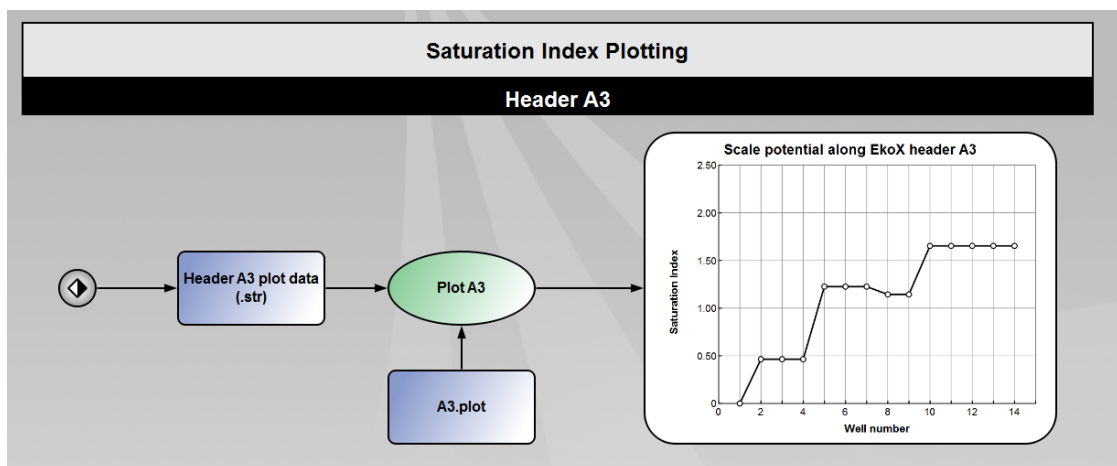


Figure 3.11 - Command-line mode plotting

3.4.5. Pipe-Itc

Pipe-Itc is a command line, non-GUI version of Pipe-It. It allows Pipe-It models to be used within any other software that can launch command-line applications. It can be also launched by Pipe-It itself, which means it allows running a project model under a command line mode. It was used at batch file which was starting scale monitoring system on different time basis and sending the generated plots to specified email address.

3.4.6. Curl

Curl is a command line tool for transferring data with URL syntax. It is free and open software that compiles and runs under a large variety of operating systems. It supports different types of files, such as (FTP, HTTP, HTTPS, IMAP, POP3, etc). Curl also supports “SSL certificates, HTTP POST, FTP uploading, HTTP form based upload” ... “proxies, cookies, authentication, file transfer resume, proxy tunneling and a busload of other useful tricks” stated at the product website. (cURL, 2013). This powerful application was used for downloading open-source information about wells and Ekofisk facilities directly from the NPD FactPages.

3.4.7. Sed

Sed is a UNIX utility, which can be used within Pipe-It. Its name is an abbreviation standing for “stream editor”, as it can parse and transform texts. Sed takes an input file processes it and outputs the modified text. It connects to the text input and reads it line by line into an internal buffer called the pattern space (GNU, 2013). And for each line set of operations, which have been specified at sed script, execute forming a cycle.

There are about 25 commands available at sed programming language which can specify the operations to be performed on the text. When the sed script ends and all operations are completed, sed write an output from the pattern space, and reads the next line, starting a new cycle. The sed script can either be specified on the command line or read from a separate file.

On example below (Figure 3.12) sed was used at scaling potential monitoring system to perform data formatting, by removing quotes from the input file.

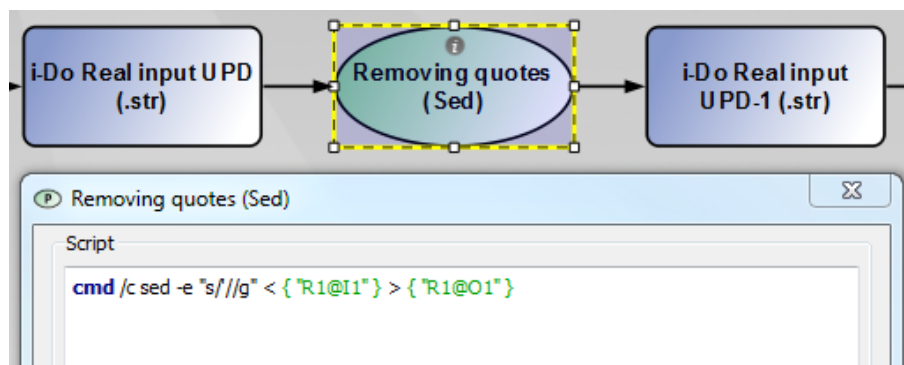


Figure 3.12 - Sed execution under command line mode

3.4.8. Gawk

Gawk (GNU awk) is a free software implementation of AWK programming language that have been created at the late seventies and distributed with version 7 UNIX (Wikipedia, 2013).

The main difference between Sed and Gawk is that, sed performs specified operations for each line; meanwhile Gawk first searches for certain patterns at each file line and only when a line have matched one of the patterns it performs specified actions on that line. Gawk keeps processing input lines in this way until it reaches the end of the input files (GNU, 1989).

To run the Gawk, user should specify its program which tells Gawk what actions should be performed on input file. The program contains series of the “rules” or commands. Each rule specifies one pattern to search for and contains one action to perform after it has found the pattern.

Gawk was used within scaling potential monitoring system to format blank cells within streamz files. Short program called “empty2zero” was written and compiled by Petrostreamz AS software developer – Gunnar Borthne and is available at Appendix H. Figure 3.13 represents Gawk integration within Pipe-It project. It uses .str input file, searches for the column name patterns specified at command line, then looks there for the blank spots and replace them with the zero.

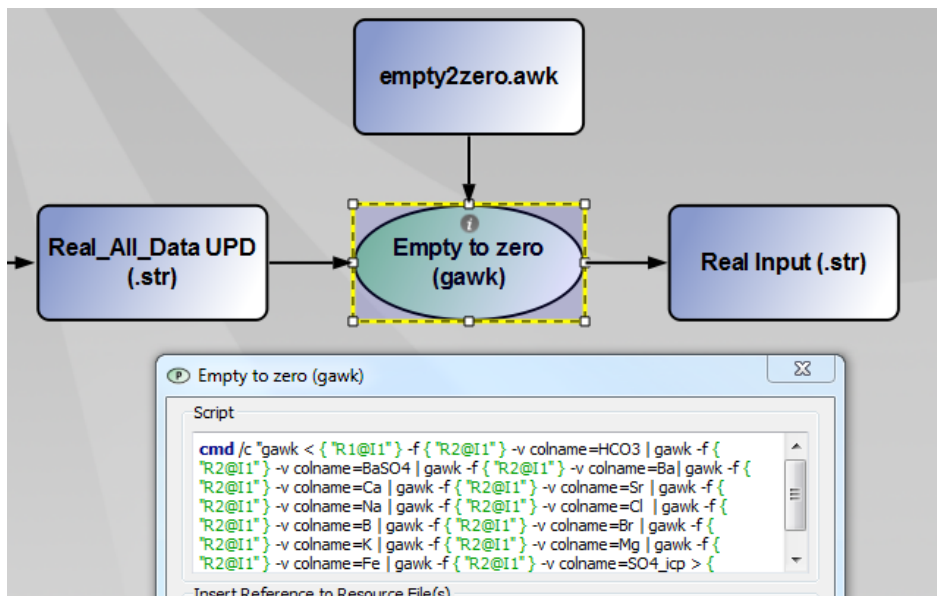


Figure 3.13 - Replacing blank streamz file cells with zeros by using Gawk

Another Gawk application also created by Gunnar Borthne is a simple modification of “empty2zero” program. It was called “zero2prev” as the main objective of this program is to search the specified column and replace cells zero values with the nonzero values from top cells. Its’ coding can be found at Appendix I.

3.4.9. PDF to JPG converter

Convert PDF to Image is open source software with simple interface specially designed to perform file conversions from PDF into image files. This tool was used in combination with Curl utility, converting downloaded by Curl PDF files into JPG format. Images contained information about different facilities and were updated every time Pipe-It started new run.

This application allows converting one or thousands of PDFs, located in one or many different folders, into a variety of different image file types (Softinterface, 2013). “PDF2JPG” is especially useful if user requires conversion jobs done on a regular basis. Conversion operation can be saved at job file where utility remembers all conversion tasks and their details. Also conversion job can be scheduled at particular time interval. “PDF2JPG” has also ability to launch other programs and perform file operations.

“Convert PDF to Image” can be run in a command-line mode without using an interface. Alternatively user can launch utility with command line execution by using operating system “command prompt” or within Windows from the START-RUN menu. Lastly, batch files (.bat) can run utility in a command line mode.

As shown on Figure 3.14 PDF2JPG was launched by Pipe-It under command-line mode. Application required one input (PDF) and one output files (JPG), which have been specified together with command arguments.

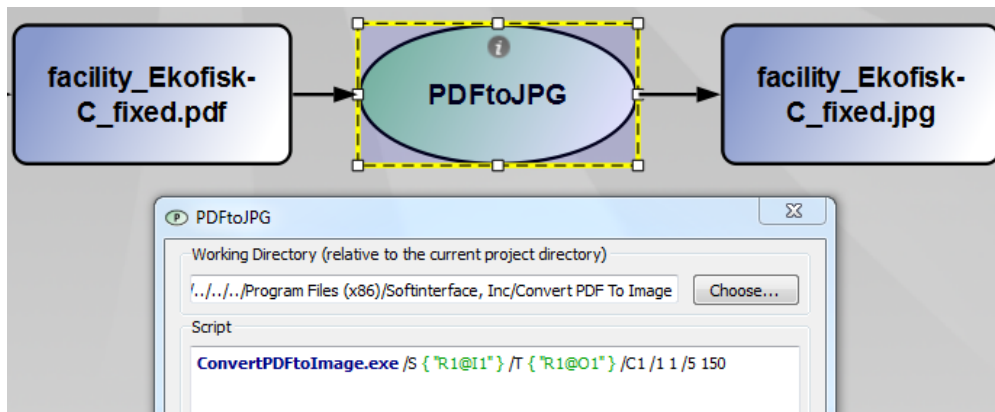


Figure 3.14 - PDF2JPG converter integration within Pipe-It

3.4.10. XML to HTM converter

This utility was created also by the same company as PDF2JPG convertor to perform conversions with Excel, text and CSV (character/comma delimited files) (Softinterface, 2013). It has the same features and can run with or without MS Excel, providing a great flexibility.

It also allows automating the process by using the built in scheduler, command line or COM/ActiveX interface. It was used within Pipe-It project to convert XLS in HTM format saving objects from XLS file as JPG images in the separate folder. Those images were further used to visualize scaling potential variation within production headers.

3.4.11. SendSMTP

SendSMTP is a small command line utility which can send SMTP email via command-line instructions or interactively (Tweddle, 2006). This useful application can send email alerts or even programmatically send files.

It utilizes Transport Layer Security (TLS) version 1.2 and SSL v2/v3 and supports different authentication methods. Password is encrypted and it runs on Windows operational system.

SendSMTP utility was used within Pipe-It to send updated plots containing scaling potential variation within production headers every time Pipe-It launched scale validation model. Figure 3.15 highlights command-line arguments needed to run SMTP utility within Pipe-It

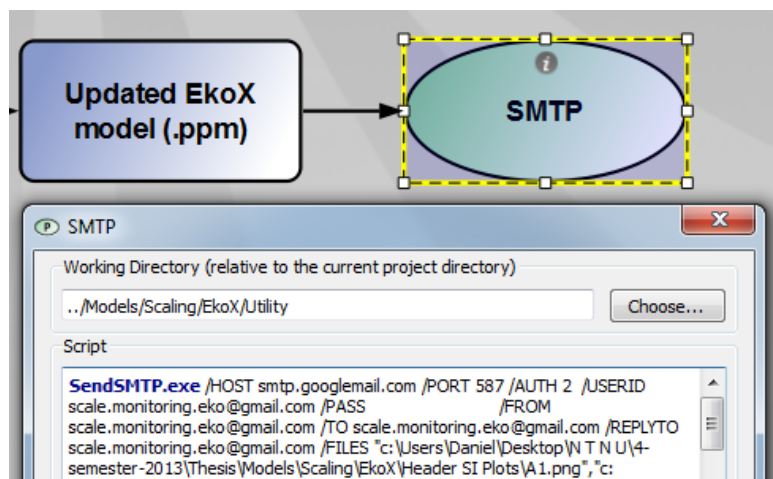


Figure 3.15 - SendSMTP utility integration within Pipe-It

All utilities and their function might be summarized under the following Table:

TABLE 9 - SOFTWARE APPLICATIONS AND UTILITIES USED WITHIN MODELS		
#	Name	Function
<i>Pipe-It built-in utilities (Streamz)</i>		
1	Copier	Split the streams in different .str files
2	Tabulator	Combine streams under one .str file
3	Txt2str	Convert .txt files in .str file
4	MapLinkz	Transfer linked data between any files
5	Strexzel	Perform defined calculations and streams manipulation
6	Plotz	Depict plots from .str file
7	Pipe-Itc	Run Pipe-It model under command-line mode
<i>Non Pipe-It utilities</i>		
8	cURL	Download required information from URL links
9	Sed	Stream editor. Utilized for modifying text files
10	Gawk	Search pattern within text and then perform operation
11	Pdf2jpg	Convert .pdf file to .jpg image under command line
12	Xml2htm	Convert .xml to .htm file, saving images from .xls
13	SendSMTP	Send email under command-line mode

3.5 Pipe-It “Table case” model

This section describes a “table case” model created within Pipe-It to validate Ekofisk-X production system for scaling potential. Ekofisk-X was selected due to some reasons. First, this is the largest production unit at Ekofisk Greater Area with 49 production wells associated with the platform. Secondly, it has similarity with production facility F5 described at Chapter 2, as it has a 50 wells associated with it. For that reason production system of F5 platform was assumed for Ekofisk-X to simulate real process calculations within Pipe-It.

Model was created within Pipe-It and contains 366 elements, from which 133 are processes, 193 are resources and 40 are composites. The outline of the system can be found at the Figure 3.16.

Model is divided by composites into different parts:

- Input data (Randomized/Real);
- Calculation of BaSO₄ saturation indices within wells;
- Calculation of BaSO₄ saturation indices within production headers;
- Plotting of saturation indices;
- Visualization of final plots.

Next sections will show the way model works describing components running within different composites/parts of the project.

Chemical treatment operations. Well routing validation for scaling potential.

Table case. EkoX Scaling Calculations

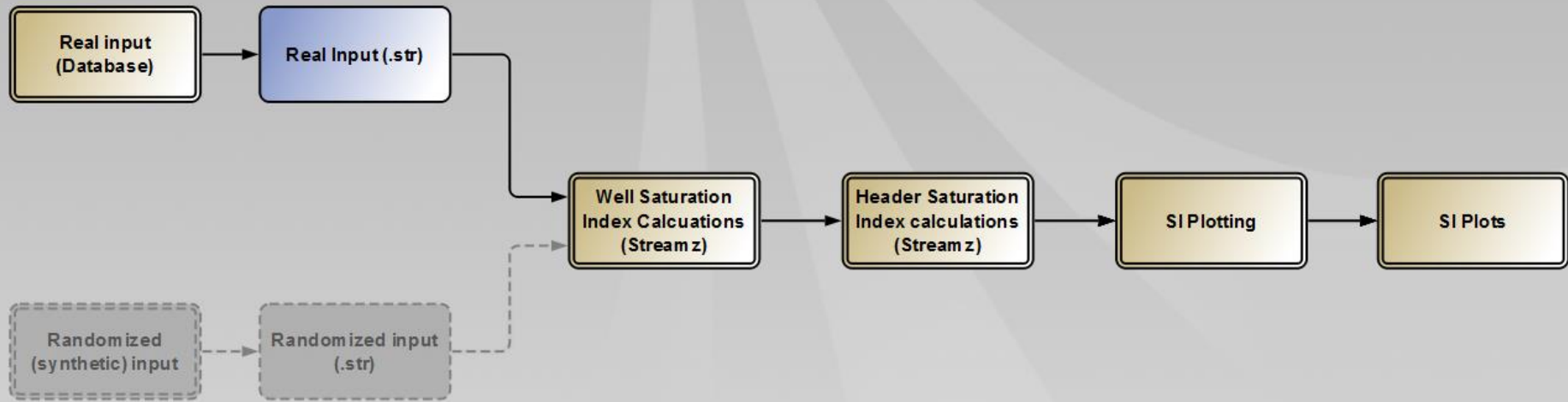


Figure 3.16 - "Table case" model for well routing validation for scaling potential at Ekofisk

3.5.1. Input data (Randomized or Real)

As was mentioned at section 3.1 there are three inputs needed to be utilized in order to validate routing for scaling potential. These are: production data (temperature, pressure and fluid rates), ion data (ionic composition of the water) and finally information regarding mixing points – facility production system and well routing.

Two options for input data are available at created systems. First, is the real input, from actual operational databases (Figure 3.17). Second, synthetic input, which is basically generated by randomization of required input parameters (Figure 3.18).

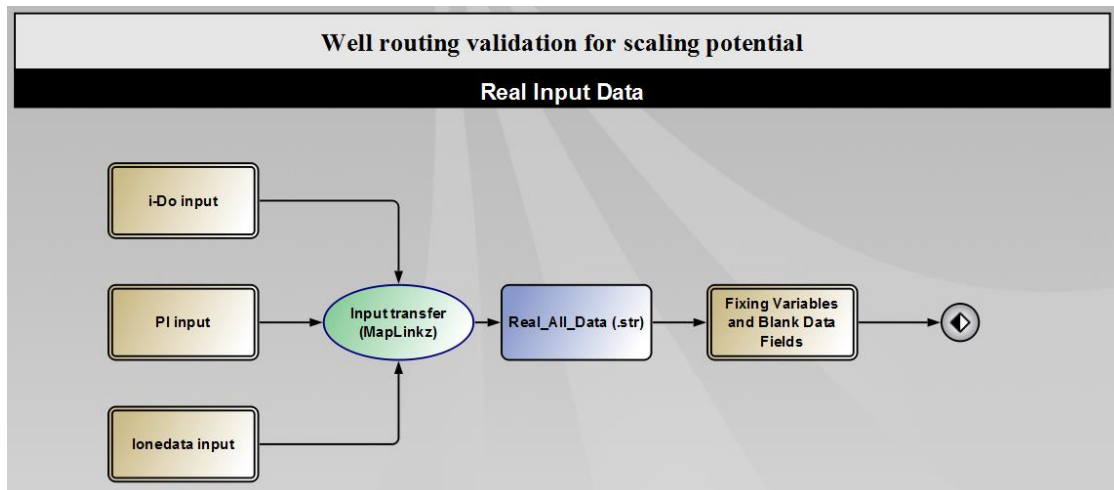


Figure 3.17 - Real input composite within Table case model

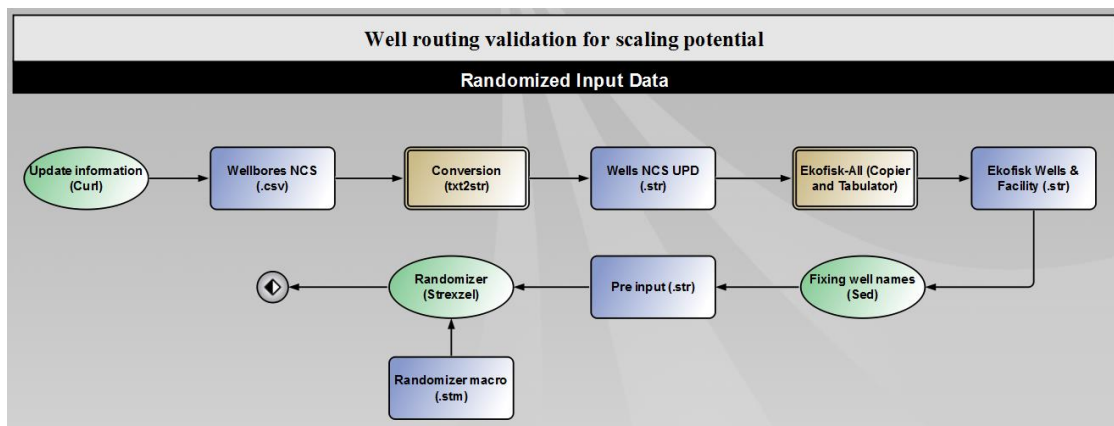


Figure 3.18 - Randomized input composite within Table case model

Real data input can be used by engineers if operational databases are available. Usually, needed input for scaling validation is stored in different places and databases. For instance, some oilfield operators use daily operations software called “I-Do”, where production data is stored and updated in real time mode (Weatherford, 2013). “PI” is other world-leading software in enterprise infrastructure for managing real-time data and events (OSIsoft, 2013). Information about well routing and production system might be located within this software application. Finally, ionic data is determined by laboratories and stored at database. Object-relational database produced by Oracle can be used for storing ionic and other laboratory measurement data (Oracle Corporation, 2013).

As can be seen production rates and conditions, ionic data and well routing are located in different databases, which can be time-consuming if validation is performed manually. Pipe-It allows automating this process and extracting required information by Linkz SQL request and saved it within .txt file located at user computer. Text file can be then transformed by txt2str utility described at section 3.4.1 into streamz file and be further used at validation procedure. As an example text file conversion and further streamz file formation which is a part of scale validation model is shown at Figure 3.19.

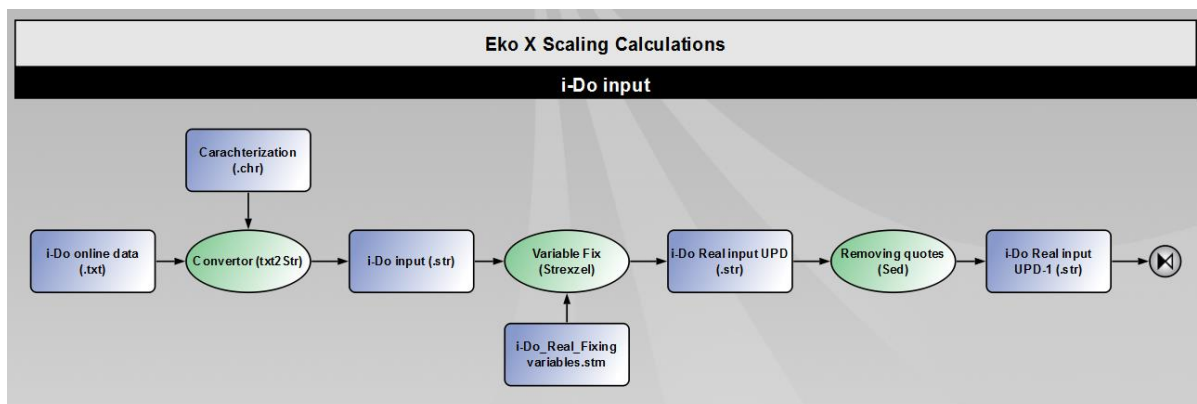


Figure 3.19 - I-Do real input conversion to streamz file

Converted text file is saved as .str file which is then used at Strexzel to fix some variables types to other format using macro file (.stm). Updated streamz file becomes an input into Sed utility, which removes quotes from string type variable to make sustainable further input data transfer (Figure 3.17) to the file containing information from all three input databases. Required information should contain “linkz” before being transferred using MapLinkz. After links are specified they are utilized within MapLinkz which combine data from three different sources. Same procedure described above is performed for PI and Ione data input files, with a bit more data formatting procedure for PI input.

After all data is transferred from three sources to one file (Real_All_Data.str) using MapLinkz, it may contain blank cells and some unusual formatting. Those problems are fixed within next composite in the system flow (Figure 3.17) by Strexzel and Gawk utilities described at previous section. Finally all information is gathered at one place – resource called “Real Input (.str)” depicted at Figure 3.16.

Before going to the next part of the monitoring system, synthetic input should be described. Figure 3.18 highlights main processes set to generate randomize input. Information about all wells from NCS is downloaded by Curl and stored at disk as CSV format file. Then table is converted by txt2str utility to streamz format file and further composite processes extract wells belonging to Ekofisk production license (Copier) also removing all unnecessary information (Tabulator). Wells name are then fixed by Sed utility to proper formatting and Randomizer macro is used within Strexzel to generate synthetic data, which is stored at file called “Randomized Input (.str)”.

User can switch between two input options by simple enabling/disabling Pipe-It elements. In case shown at Figure 3.16 real data is used as input to monitoring system.

3.5.2. Calculation of BaSO₄ saturation indices within wells

Grey circles represent the connections between different project levels (Figure 3.20). Information from real input (top connector) or randomized input (bottom connector) is transferred to Ekofisk-X (EkoX) wells Copier utility. It extracts wells data associated with EkoX and stores it in a streamz file. Oddo-Tomson calculations are performed for EkoX wells within next process item. Strexzel uses macro file with predefined formulas and operations to calculate saturation index for each well and saves output information in the streamz file used at the next composite for scaling calculations within production headers.

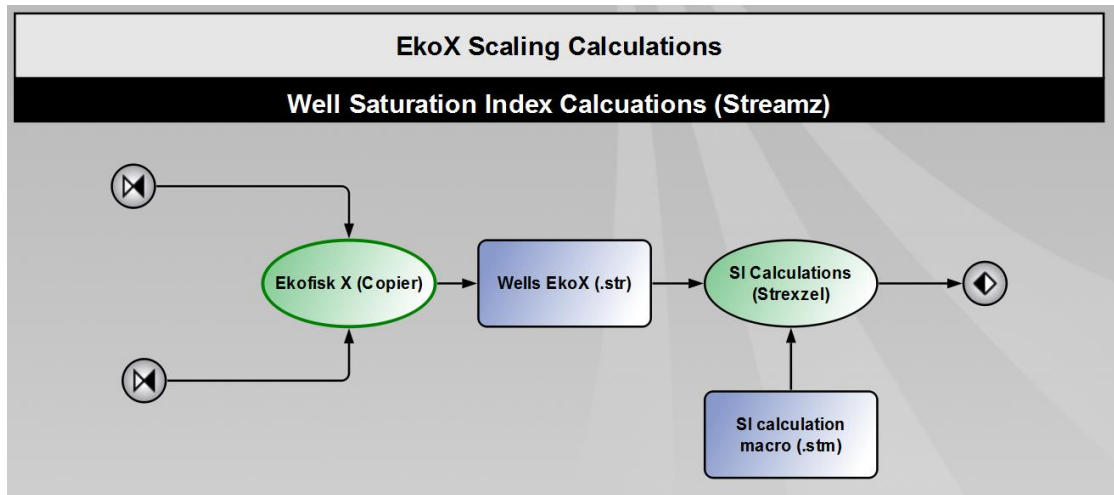


Figure 3.20 - Wells saturation indices calculation within Pipe-It

3.5.3. Calculation of BaSO₄ saturation indices within production headers

Next composite at Figure 3.16 reproduce assumed production system of the EkoX and perform SI calculations. Fluids coming out the wells are mixed at manifolds which are the parts of production headers. Figure 3.21 shows assumed production system of EkoX with four headers and two manifold options for each header.

Processed streamz file data from wells SI calculation composite is split using Copier between four headers. Each header has a number of associated wells connected to it in fixed sequence (Figure 3.22). Using Tabulator wells become connected to each other in order they are connected in a real life forming header data streamz output file. As each header has two associated manifolds, it can be routed to HP or LP manifolds by specifying filter names at HP or LP Copier. Routing will be changed every time within databases, but well connection order will stay permanent. Eventually 8 generated streamz files (4 headers with 2 routing options each) are used at saturation indices calculation (Figure 3.23). Macro file is used within Strexzel to perform those calculations. Macro coding can be found at Appendix J. Calculated results are stored and further processed with data formatting as the final output file have to reflect development of scaling potential within each header. If wells were routed to another manifold its SI value will be assigned to zero, that is the reason why Gawk program zero2prev was utilized for. It replaces those zeros with SI values from previously connected wells. Finally, formatted streamz files are transferred to plotting composite.

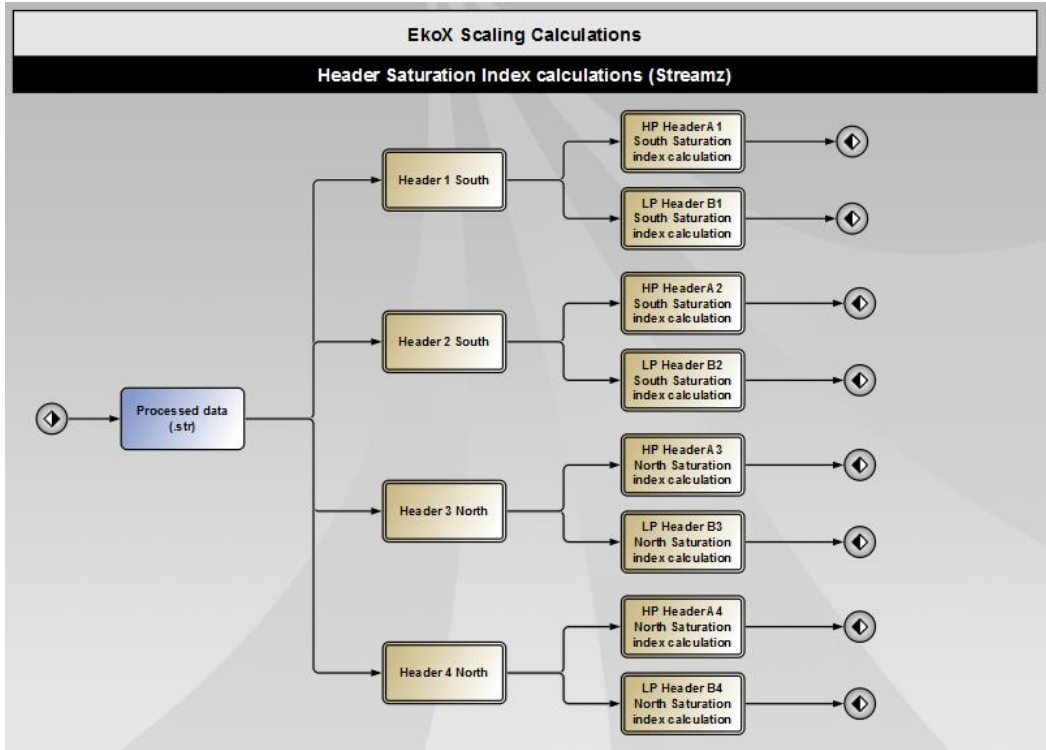


Figure 3.21 - Production headers saturation indices calculation within Pipe-It

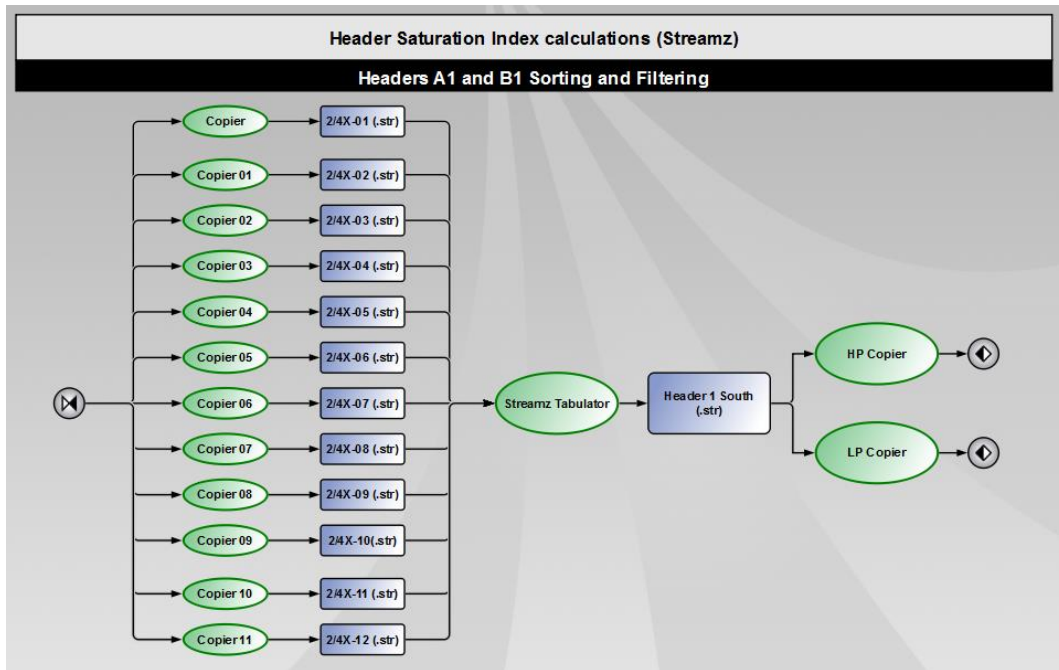


Figure 3.22 - Production header 1 data sorting and filtering within Pipe-It

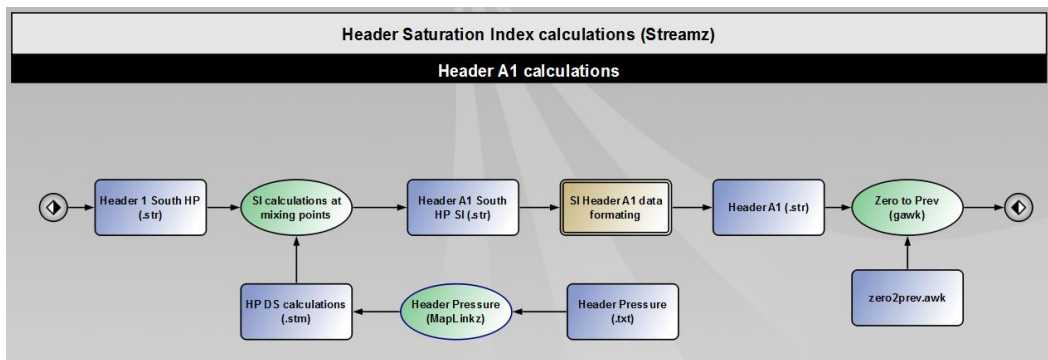


Figure 3.23 - Manifold SI calculations

3.5.4. Plotting of saturation indices

Streamz files containing scale potential development within production headers are sent to plotting composites (Figure 3.24). Inside those composites .str file is used as input to the utility called “Plotz” (Figure 3.25). Together with the predefined plot structure (.plot file) they allow Plotz to generate output plot which is then stored and visualized in the next composite.

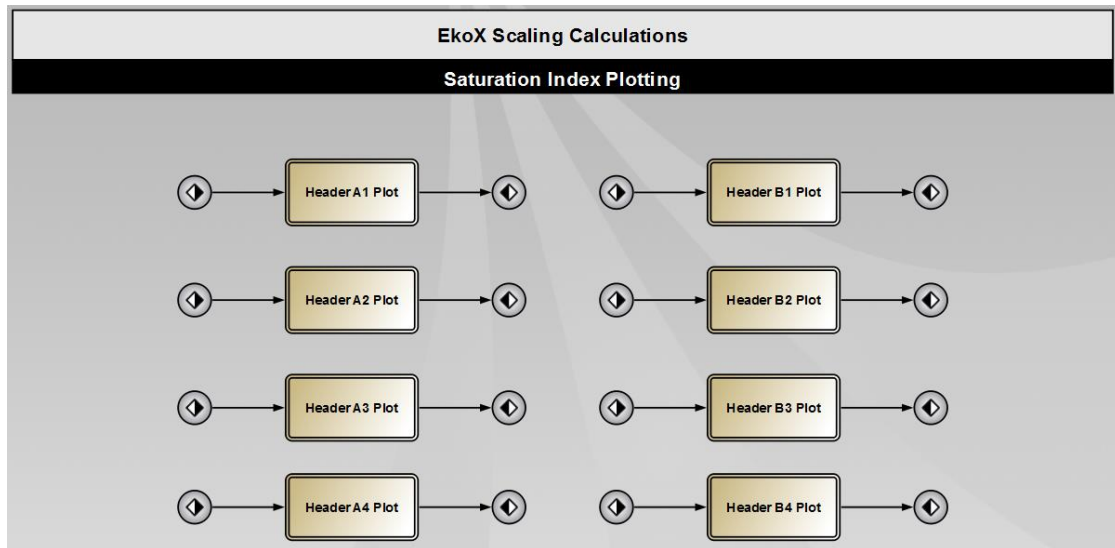


Figure 3.24 - Plotting of scale potentials within Pipe-It

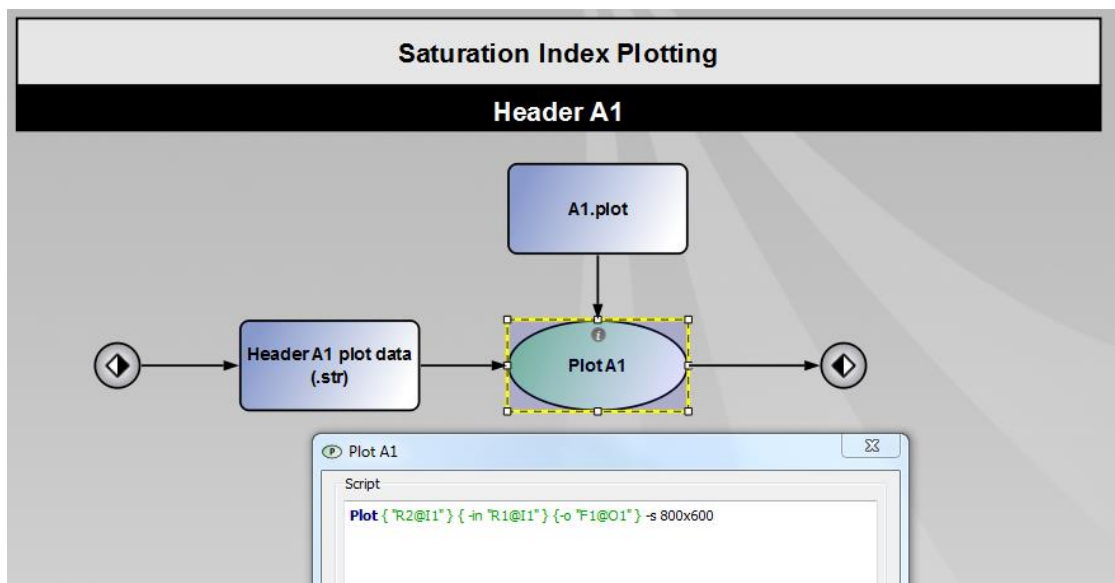


Figure 3.25 - Plotz utility

3.5.5. Visualization of final plots

Generated plots are saved at disk and can be visualized at Pipe-It canvas. Resource properties can be specified by user and any picture or other file can be assigned to the background of the item. Figure 3.26 depicts final plots of scaling potential build-up within production headers. This will provide information to production chemists about possible scaling problems and places where they might occur. Enormous potential of scale deposition can be detected by monitoring system and preventive operations performed.

Monitoring system can be used to evaluate well routing for scaling potential and provide a feedback to production engineers.

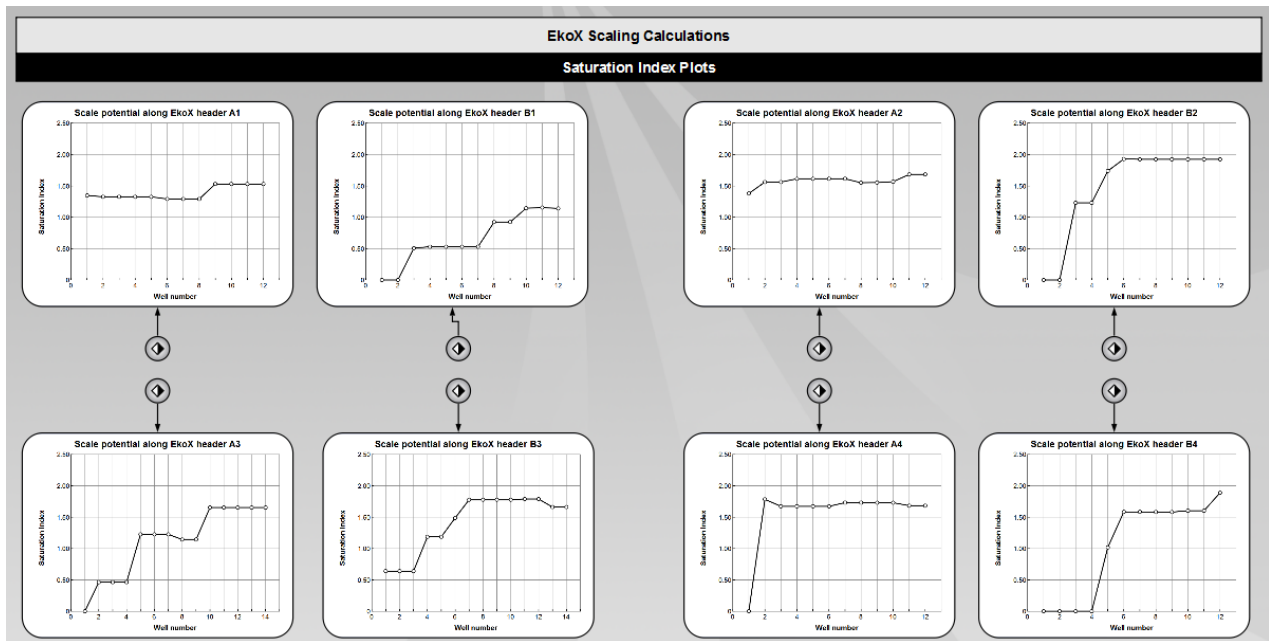


Figure 3.26 - Scale potential plots within Pipe-It

3.5.6. Self-triggering scale monitoring system

Developed scale monitoring system was used at Pipe-It master project in combination with SMTP utility (Figure 3.27), which purpose was to run and update monitoring model and then send updated plots to specified email address. Master project can be launched by batch file through command-line mode. Created batch file was implemented within Windows Task Scheduler to execute master project on daily basis at specified time.

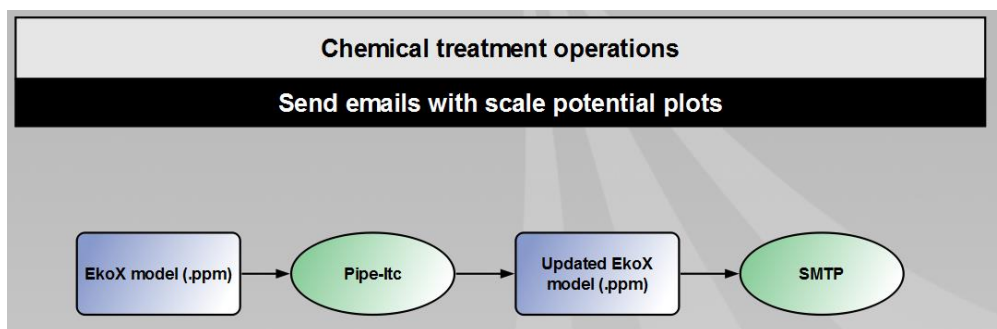


Figure 3.27 - Sending updated plots using SMTP utility

3.6 Pipe-It “Visual case” model

This section describes a “visual case” model created within Pipe-It for visualization of scaling monitoring system at EkoX. “A good sketch is better than a long speech”, Napoleon Bonaparte said. Visualization makes possible to absorb quickly large amounts of data, meanwhile table data format is not much convenient to perceive information.

Created model has a same concept as a “table case” monitoring procedure plus some additional features. Visualized model was also created within Pipe-It and has more elements than table model due to visualization of entire Ekofisk oilfield infrastructure. It includes 739 elements, from which 134 are processes, 483 are resources and 122 are composites. The visualization of Ekofisk oilfield and implementation of scale potential monitoring system can be found at the Figure 3.28.

3.6.1. Multi-level structure of the visual model

Basically model structure has a multi-level organization.

1. Top level. It represents asset with all facilities related to it;
2. Midlevel. It comprises particular facility and might be used for modeling of topside operations performed at this facility;
3. Bottom level. Third is a subsea level with the well data and its placement.

Asset level was already shown at Figure 3.29 and includes facility composites and brief information about Ekofisk obtained from ConocoPhillips – operator company website (ConocoPhillips Norge, 2013). All composites except composite “Input data” represent real platform. Data composite is not referred to real object, but is placed on the canvas to represent data transfer from the top to the bottom levels.

Midlevel contains information about facility and topside processes associated with it. Platform picture and description were taken from operators’ website. Figure 3.30 depicts Ekofisk-X with four production headers (A-B manifolds are related to particular header) and a separate composite for scaling monitoring system. Table with information about facility at top right corner is a composite background image. Inside composite Pipe-It download data from the NPD FactPages using Curl and then file is converted to JPG format using PDF2JPG utility. Each time Pipe-It runs visual model information about facility is updated and can be easily seen from canvas. Figure 3.28 represents composite processes.

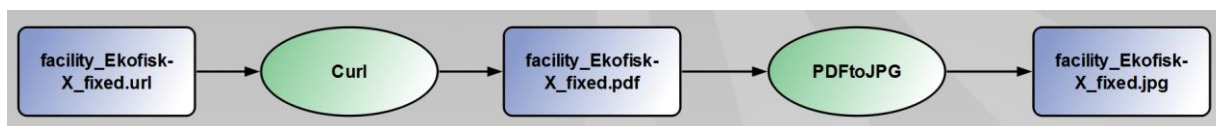


Figure 3.28 - Platform information updating process within Pipe-It

Bottom level represents part of facility production system. It contains well, its location and associated data, production header and manifolds representations. Well placement was found at NPD FactPages map; data is transferred from “Input Data” composite located at asset level. Bottom level of visual model is shown at Figure 3.31. Each well composite contains a streamz file with related data for that particular well and a resource with URL link to the well webpage at FactPages. User can have a fast access to get information about this well by double clicking at the resource.

Foto : Kjetil Alsvik / ConocoPhillips

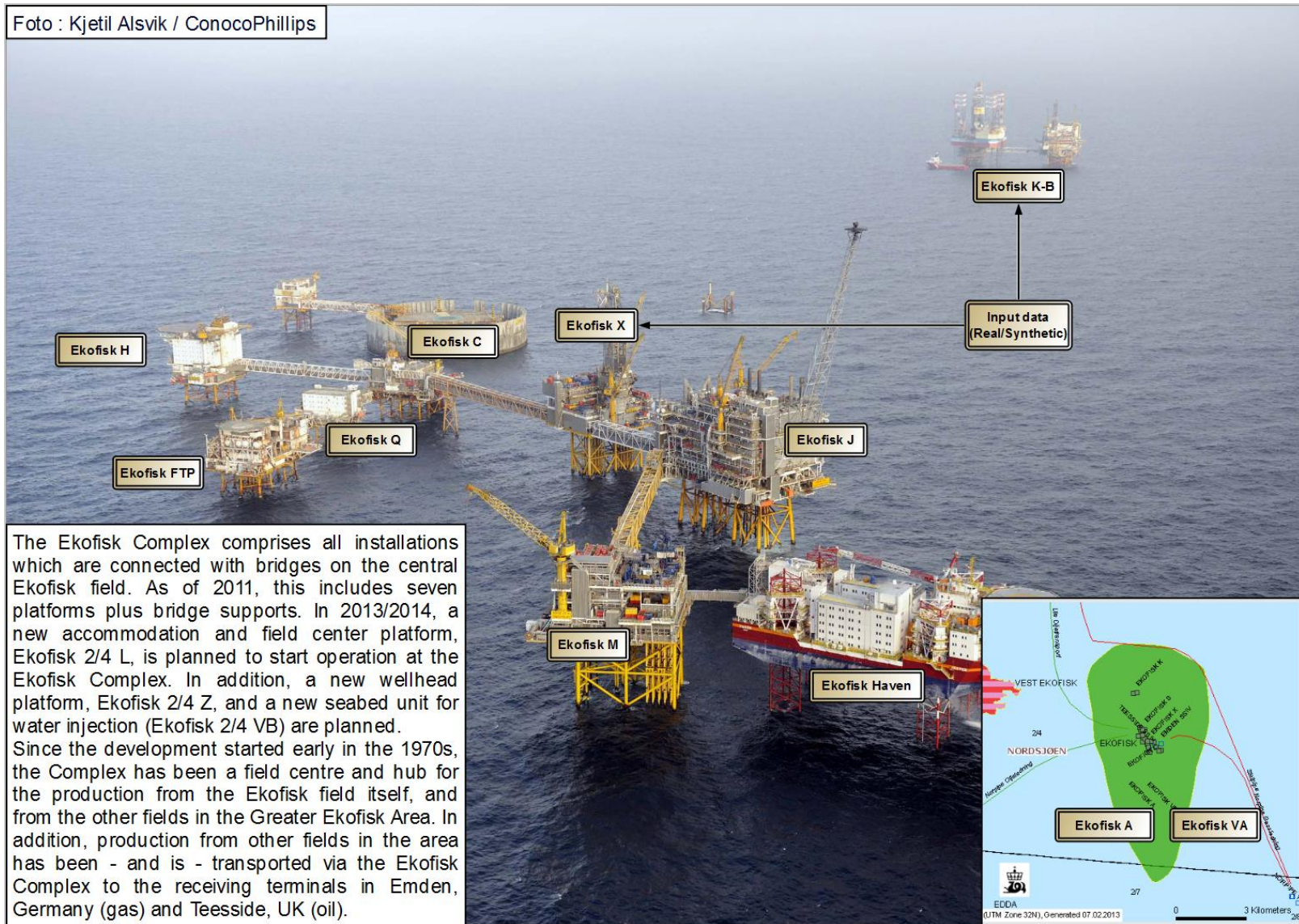


Figure 3.29 - Visualization of Ekofisk oilfield and implementation of scale potential monitoring system

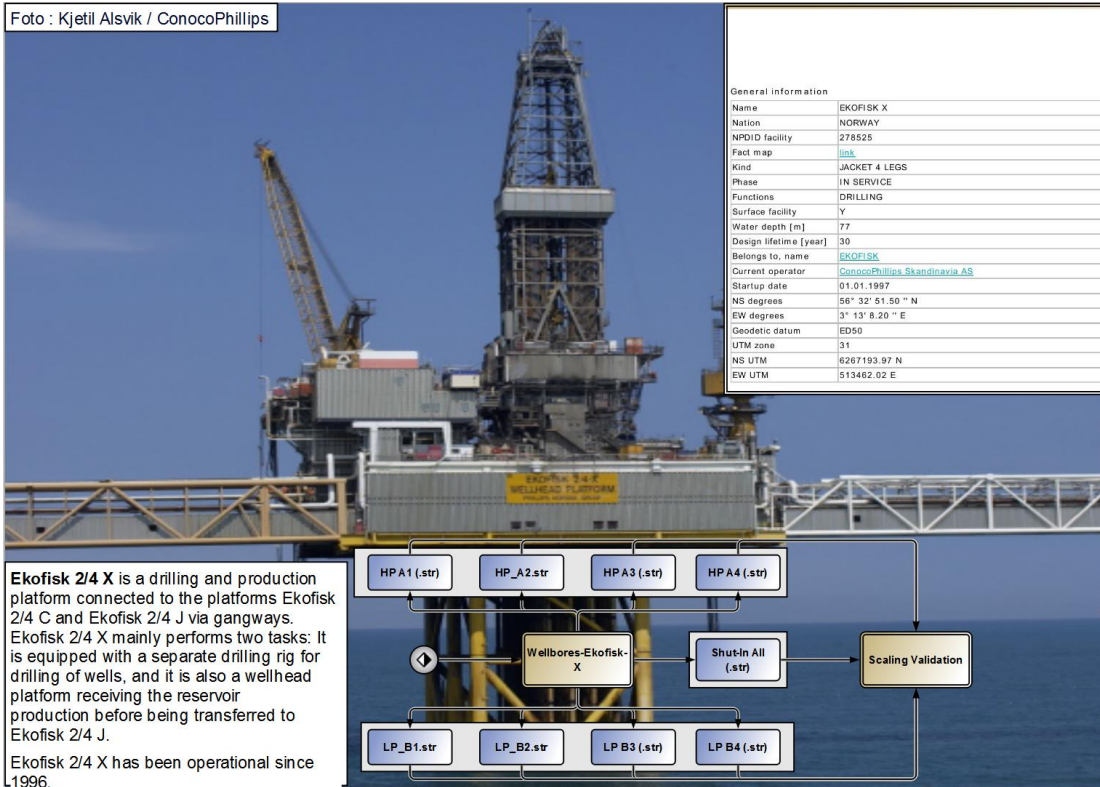


Figure 3.30 - Ekofisk-X topside visualization

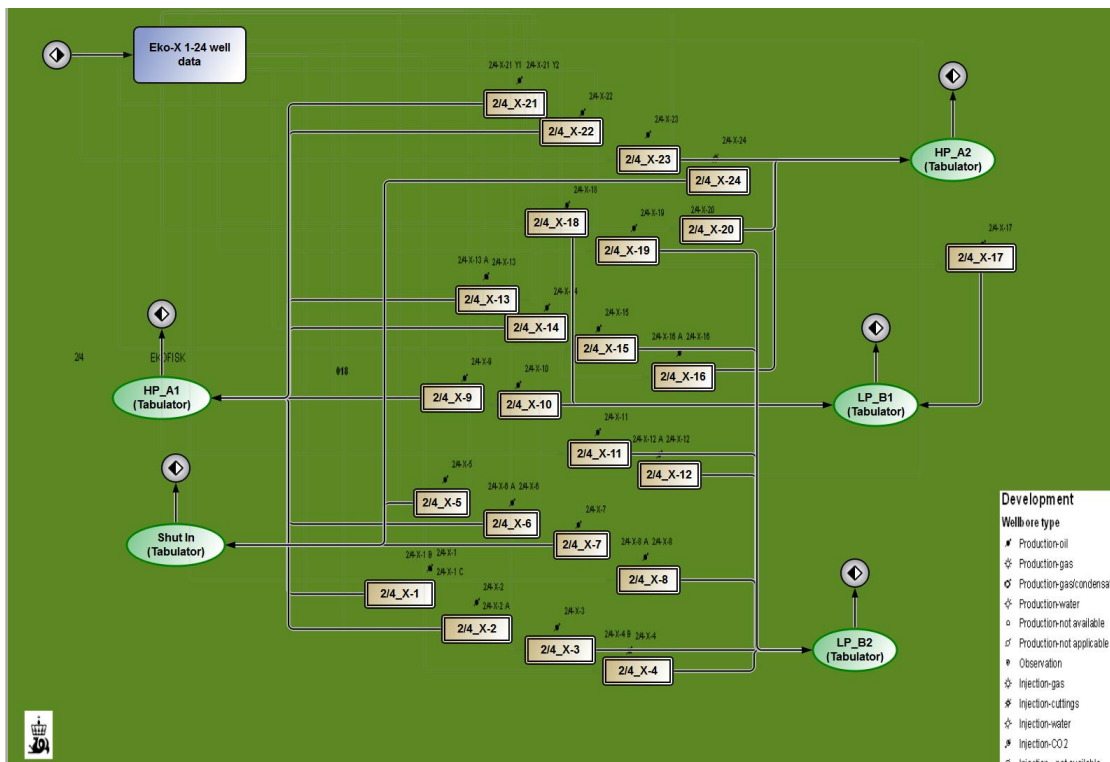


Figure 3.31 - Visual case model bottom level

3.6.2. Input data (Randomized + Real)

Input data is transferred to the well level from the asset level and then tabulated and transferred back to the topside level to represent production streams going from the wells to the platform. Data is generated for entire oilfield in a same way as within “Table case” model. After being created, entire dataset splits by Copier to streamz files related to particular facility (Figure 3.32). Information streams are then sent to the well level (for instance EkoX and EkoB) where they are tabulated regarding well routing representing real process and sent to the topside level. Randomized input option is also available for this model and works in a same way as at table model.

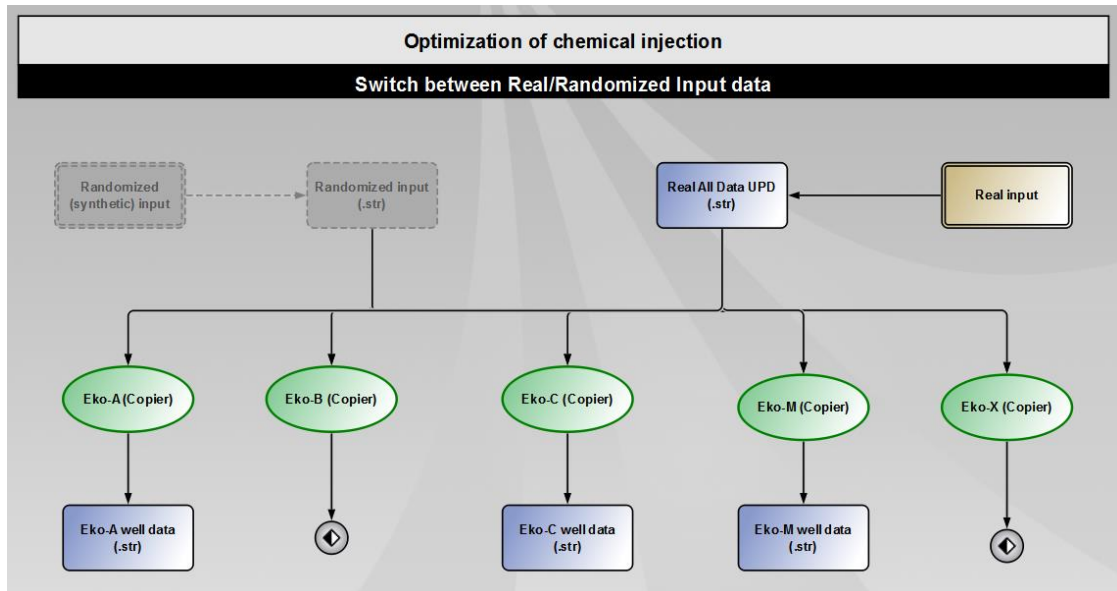


Figure 3.32 - Input data information flow. Visual model

3.6.3. Scaling potential validation procedure

Scaling validation is performed with the same concept as for table case model. Excel sheet with the same Odco-Tomson calculation procedure was used and results obtained by different applications were compared. Excel version of scale monitoring system requires manual data input from three sources: I-Do, PI and Ione data. Pipe-It was used to automatize this process. Data from well headers were tabulated at one file and transferred to Excel sheet using MapLinkz. Output information was used for visualization by two methods. First, extracting plots from XLS file by converting it to HTM format. While file is converting, associated folder with all images is also saved at the disk and images can be further used at Pipe-It canvas (Figure 3.34). Second visualization approach uses Plotz utility to visualize scaling potential plots.

Comparing two methods it should be noted, that table model runs faster and requires only 12 seconds per run. Meanwhile visual case needs 1 minute 16 seconds per run from which 42 is used to input and output results from Excel sheet and 15 seconds for XLS2HTM utility to convert spreadsheet and save images.

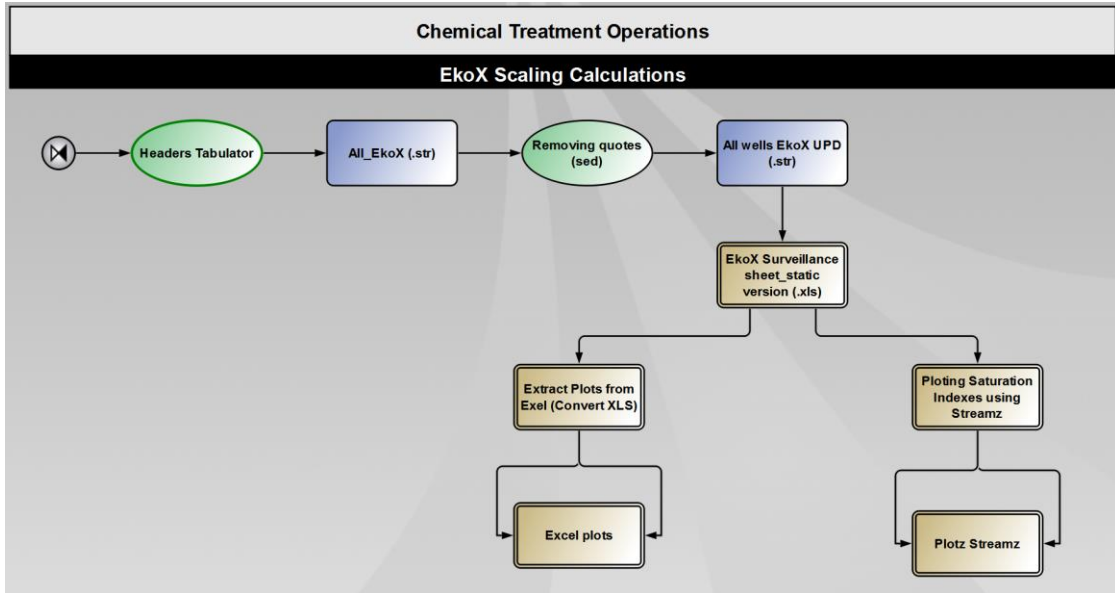


Figure 3.33 - Scale validation procedure at Visual Case model

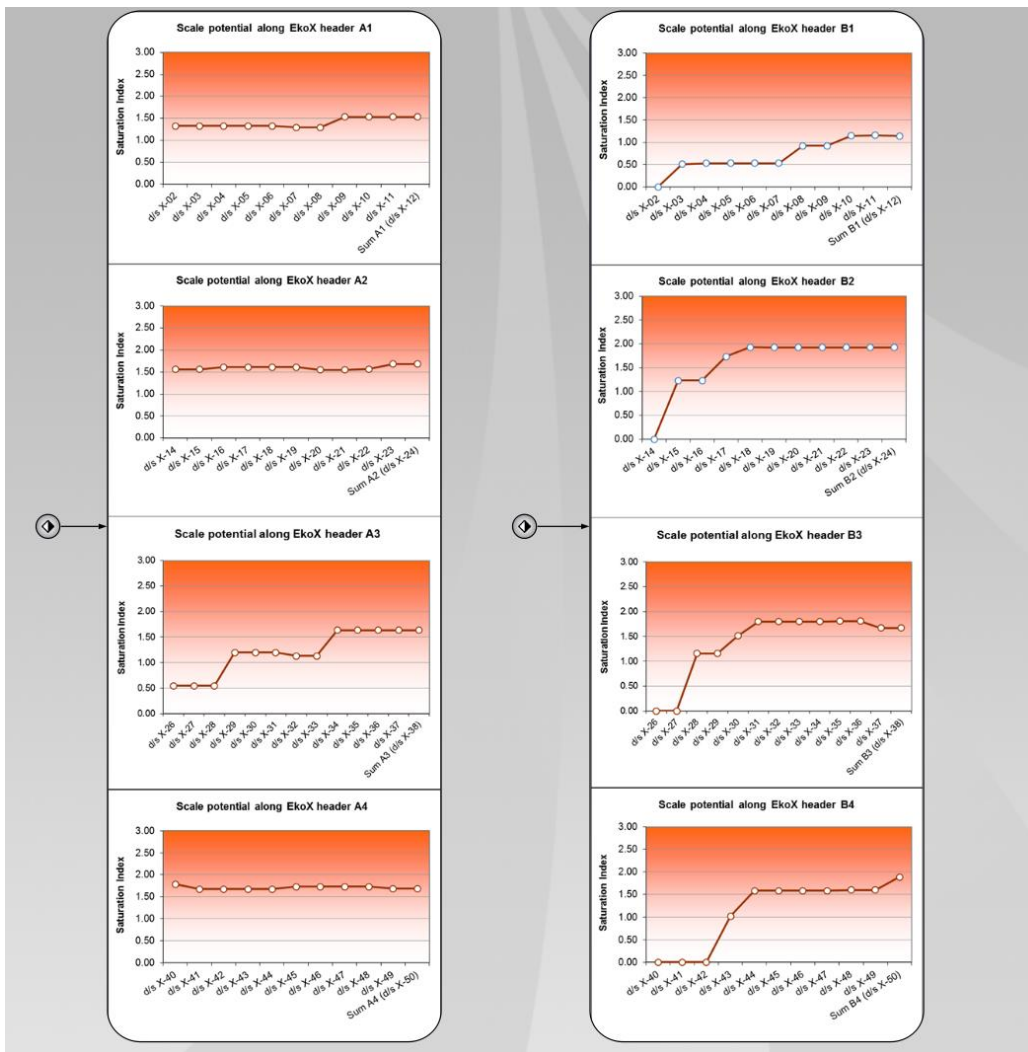


Figure 3.34 - Excel plots from Visual model

3.7 Models comparison and further development

Models results were compared in order to see the difference between Streamz and Excel calculation results. From the Figure 3.35 it can be easily seen that results were identical. Also model sustainability has to be further tested using links to the actual databases, as far as data formatting within databases could vary.

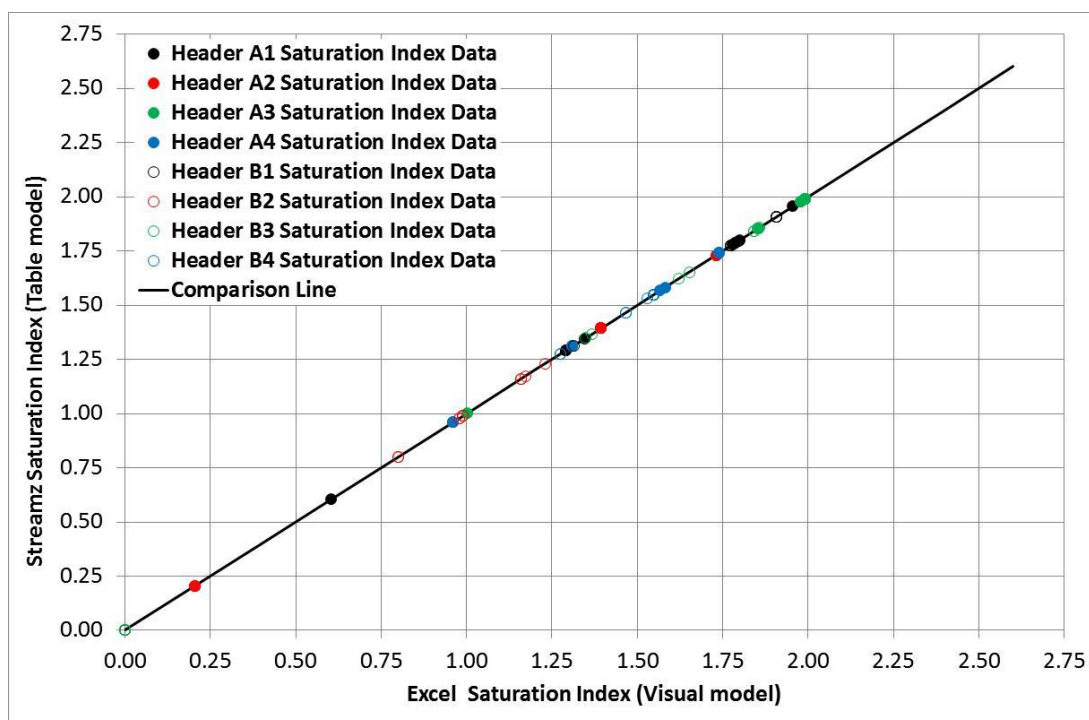


Figure 3.35 - Comparison of Table and Visual case model results.

Based on example of created monitoring system for Ekofisk-X, Pipe-It project can be further developed in different ways:

- Create same monitoring system for other platforms and facilities within Ekofisk or even for other oil and gas field where scaling is an issue;
- Develop a scaling inhibitor dosage model based on laboratory results and use it within Pipe-It to optimize chemical dosage and prevent scaling during production;
- Create a complex chemical treatment system by “one by one” integration within Pipe-It project other production monitoring systems or models for chemical treatment operations described at chapter two:
 - Corrosion rate monitoring and inhibitor treatment;
 - H₂S & O₂ scavengers treatment;
 - Emulsion breaker treatment ;
 - Flocculant treatment ;
 - Antifoam treatment ;
 - Biocide treatment;
- Optimize monthly well test schedule. Each well has to be routed to the test separator once a month, by keeping scaling potential at minimal level Pipe-It can create optimized well test schedule;
- Integrate monitoring system within any production forecaster to validate well routing for scaling potential.

4 CONCLUSIONS

- (1) It is really necessary to monitor production conditions and composition of produced fluids at each mixing or specified point in order to predict occurrence of particular issue and evaluate effectiveness of applied chemicals, as far as majority of reagents can show good performance only within specific conditions.
- (2) Production chemicals used for solving different issues and their concentrations should be carefully chosen before being applied for the field operations otherwise they can hinder each other performance.
- (3) Based on integration example of scaling potential monitoring system within Pipe-It project it can be stated that integrative chemical treatment management system can be developed providing fast, better understanding of chemical impact and evaluation of chemical performance.
- (4) Created Table case model is a robust, fast and simple approach to monitor scaling potential within production headers and point at places with enormous values of scaling potential.
- (5) Oddo-Tomson calculations are performed 6 times faster using Streamz technology instead of common Excel file utilization, which makes Streamz favorable for execution and optimization purposes.
- (6) Developed models reproduce sustainable results within Pipe-It project and allow reducing time-consuming work of updating Excel sheet manually.
- (7) This work highlights a potential to create a complex integrated chemical treatment operations system. Scaling potential monitoring models are the first steps in a way to develop this system and further work can be done to solve new problems and model another production issues.

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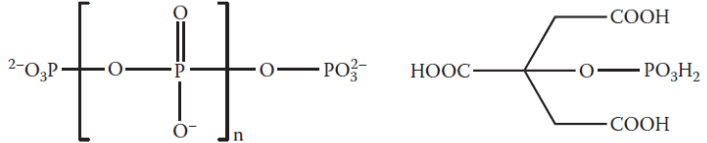
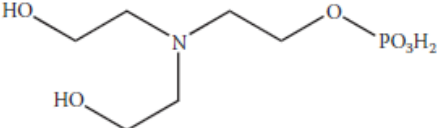
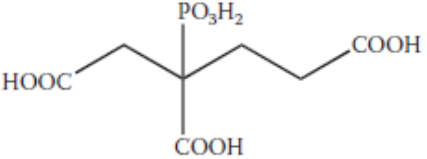
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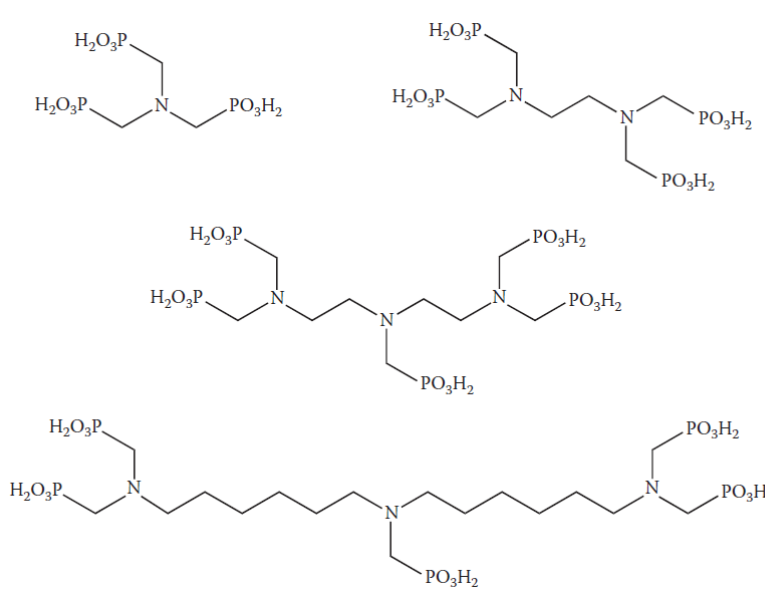
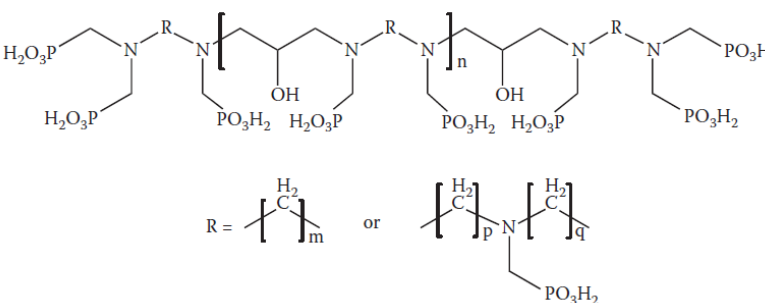
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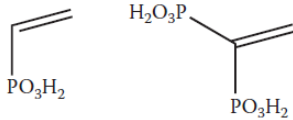
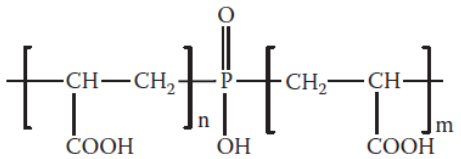
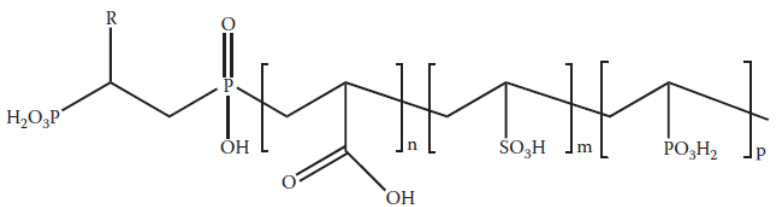
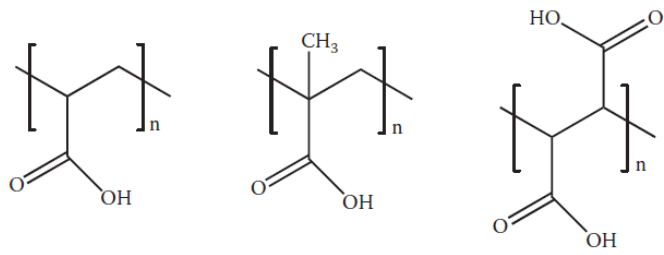
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6 APPENDIX A – SCALING INHIBITORS

TABLE 10 - CARBONATE AND SULPHATES SCALE INHIBITORS

№	Classes of scale inhibitors	Chemicals	Purpose and effect	Features
1	Polyphosphates	 <p>The figure shows two chemical structures. On the left is the polyphosphate anion, represented as a chain of phosphorus atoms connected by oxygen atoms, with terminal phosphate groups having a negative charge. On the right is citric acid phosphate, which consists of a central carbon atom bonded to three hydroxyl groups and one phosphate group.</p> <p>Figure 6.1 - Polyphosphate anion and citric acid phosphate respectively</p>	<p>Calcium carbonate scale inhibitors. Also has some activity as a corrosion inhibitor. Some chemicals can be used for BaSO₄ scale inhibition.</p>	<p>More thermally stable and more compatible products for oilfield scale inhibitors. Mainly used in boiler water treatment at low Ca concentrations.</p>
2	Phosphate esters (ROPO ₃ H ₂)	 <p>The figure shows the chemical structure of triethanolamine phosphate ester, which consists of a central nitrogen atom bonded to three hydroxyl groups and one phosphate group.</p> <p>Figure 6.2 - Triethanolamine phosphate ester</p>	<p>Calcium carbonate and calcium sulfate scale inhibitors. Also show corrosion inhibition activity. If conditions are not very acidic, could be used for BaSO₄ scale inhibition.</p>	<p>Environment-friendly scale inhibitors. Could be water- or oil- soluble. Compatible with high-calcium brines. Have limited thermal stability up to 95°C for topside application (sulfate scale) and 110°C (carbonate scale)</p>
3	Nonpolymeric Phosphonates and Aminophosphonates	 <p>The figure shows the chemical structure of 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), which consists of a four-carbon chain with a phosphate group on the second carbon and carboxylic acid groups on the first, second, and fourth carbons.</p> <p>Figure 6.3 - 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA)</p>	<p>Calcium carbonate scale inhibitor. Salts of PBTCA are sulfate scale dissolvers.</p>	<p>Phosphonates tend to have a lower “cutoff” temperature than polymeric scale inhibitors. PBTCA related molecule - Phosphosuccinic acid converted to its’ easter performs good inhibition and is oil-soluble, which also can function as asphaltene dispersant. Discharges of phospho-</p>

	 <p>Figure 6.4 - Aminotris(methylenephosphonic acid) ATMP, 1,2-diaminoethanetetakis(methylenephosphonic acid) EDTMP, diethylenetriaminepentakis(methylenephosphonic acid) DTPMP, and dihexamethylenetriaminepentakis(methylenephosphonic acid) DHTMP</p>	<p>-NH₂-CPO(OH)₂ increases the metal binding ability. Calcium carbonate and calcium sulfate scale inhibitors.</p>	<p>nates can lead to unwanted eutrophication in lakes and coastal areas. ATMP is the simple and cheap inhibitor, but not very effective. DTPMP is an excellent carbonate and sulfate scale inhibitor, most used in the oil industry. DTHMP doesn't precipitate in high calcium content and is useful for high-temperature applications of 120 to > 140°C. Majority of aminophosphonates have low biodegradability but they are low in toxicity and bioaccumulation. Low molecular weight phosphonates has been found environmentally acceptable.</p>
<p>4 Polyphosphonates: (a) with polyamines backbone and (b) with polyvinyl backbone</p>	 <p>Figure 6.5 - N-phosphonomethylated amino-2-hydroxypropylene polymers (a)</p>	<p>Barite scale inhibitor. Squeeze applications.</p>	<p>Molecular weight about 300-5000.</p>

		 <p>Figure 6.6 - Vinyl phosphonic acid (VPA) and vinyl diposphonic acid monomers (VDPA) (b)</p>	Copolymers of VPA with unsaturated dicarboxylic anhydrides – barium and strontium scale inhibitor.	VPA and VPDA are fairly expensive, that is why they are converted to the next type of chemicals (5).
5	Phosphino Polymers and Polyphosphinates	 <p>Figure 6.7 - Polyphosphinocarboxylic acid (PPCA)</p>  <p>Figure 6.8 - Phosphonate-end-capped polymers</p>	Carbonate scale squeeze inhibitors. Barite scale inhibitor.	PPCA perform better for barium sulfate, have larger calcium compatibility and squeeze lifetime. Phosphonate-end-capped phosphine polymers (Fig. 6.8) are particularly useful for barite scale, show good rock adsorption and better thermal stability. They have over twenty percent of biodegradability.
6	Polycarboxylates based on: (a) Polyacrylic acid (b) Polymethacrylic acid (c) Polymaleic acid	 <p>Figure 6.9 - Polyacrylic (a), polymethacrylic (b), and polymaleic acids (c)</p>	Salts of polycarboxylic acids are scale inhibitors. Maleic acid copolymers (CP) with hydrophobic monomers are barium and strontium scale inhibitors.	Polyacrylates are mainly poor biodegradable, but some can be fairly biodegradable. Most polymers have Mw 1000-30000. To improve high calcium tolerance sulfonated groups could be introduced. To increase squeeze lifetime quaternary amine monomer can be incorporated. Acrylic CP with cationic monomer will also have biocide and corrosion inhibitor properties.

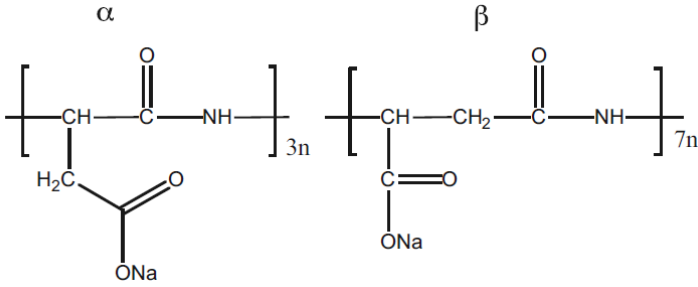
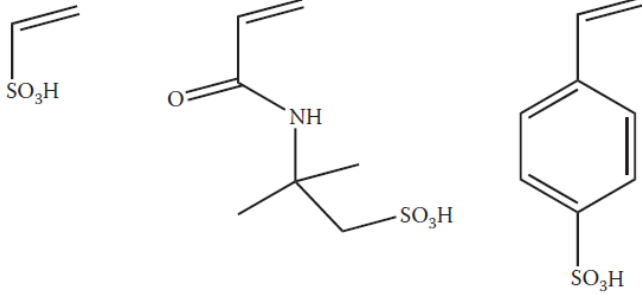
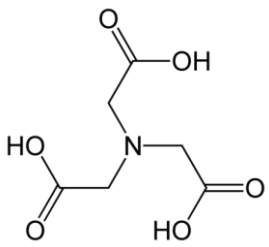
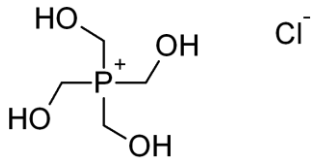
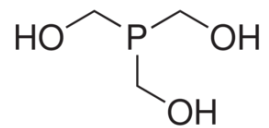
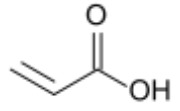
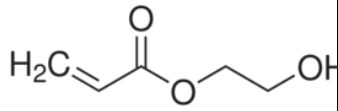
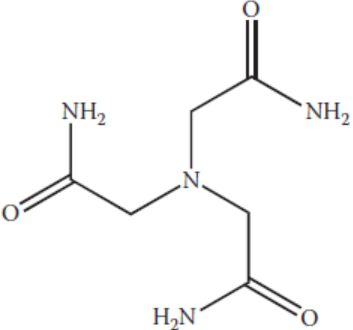
6.1	Biodegradable Polycarboxylate	 <p style="text-align: center;">Figure 6.10 - Sodium polyaspartate. $R\alpha/\beta$ is approximately 3:7</p>	<p>Carbonate and Sulfate scale inhibitors.</p> <p>Highly biodegradable.</p> <p>Good performance.</p> <p>Some chemicals of this type are known as fairly low-toxicity corrosion inhibitors.</p>	<p>Polyaspartate (PA) is used in regions where biodegradability should be higher than 20%. Used in squeeze treatments at up to 85 °C (185 °F).</p> <p>PA reduces fines migration after a squeeze treatment. Could be biosynthesized downhole (<i>in situ</i>) by injection of genetically engineered, thermophilic microorganisms and suitable nutrients.</p>
7	Polysulfonates	 <p style="text-align: center;">Figure 6.11 - Vinyl sulfonic acid (left), acrylamido(methyl)propylsulfonic acid (middle) and styrene sulfonic acid (right)</p>	<p>Show best performance against barite scale. Inhibit sulfate scales.</p>	<p>Polysulfonates can work as scale inhibitors at lower pH values.</p> <p>Due to high thermal stability and calcium tolerance they have been used for high-temperature squeeze applications for sulfate scale.</p> <p>Squeeze lifetime is shorter with these polymers due to weaker rock adsorption.</p>

TABLE 11 - SULPHIDE AND HALITE SCALE INHIBITORS

№	Classes of scale inhibitors	Chemicals	Purpose and effect	Features
1	Aminocarboxylate chelates	 <p align="center">Figure 6.12 - Nitrilotriacetic acid (NTAA)</p>	Prevent iron sulfide scaling in moderate temperature wells by sequestering iron. Usually utilized at sour gas wells.	Weak performance at high temperature applications. Should be added in stoichiometric amounts to dissolved iron. Could be very corrosive for the production equipment.
2	Phosphines	 <p align="center">Figure 6.13 - Tetrakis(hydroxymethyl)phosphonium chloride (THPS)</p>  <p align="center">Figure 6.14 - Tris(hydroxymethyl)phosphines (THP)</p>	Inhibition and solubilization of iron sulfide scale.	Blends of phosphines with ammonia or small primary amine (methyl amine) will prevent polymerization side reactions at low pH.
3	Copolymers of hydroxyethylacrylate/acrylic acid	 <p align="center">Figure 6.15 - Acrylic acid</p>  <p align="center">Figure 6.16 - 2-hydroxyethyl acrylate</p>	Zinc sulfide threshold inhibitor.	Has to inhibition mechanisms: (a) Inhibition due to inhibitor lowering of the pH or (b) Threshold scale inhibition.

4	Hexacyanoferrate salts	$M_3[Fe(CN)_6] \text{ M=Na or K}$ <p>Figure 6.17 - Hexacyanoferrate salts (HCF)</p>	Modifier of halite crystals. Significantly inhibits halite crystallization.	HCF increases level of critical supersaturation within solution and modifies the halite crystals. Then they are easily removed by periodical washing with low salinity water. To avoid HCF deactivation reaction with Fe^{3+} salts sequestering agents can be added.
5	Nitrilotrialkanamides and quaternary salts	 <p>Figure 6.18 - Nitrilotriacetamide</p>	Halite precipitation inhibitor	Nitrilotriacetamide (Figure 6.18) has high temperature stability and is biodegradable. Have been successfully used for topside operations and downhole in squeeze treatment.

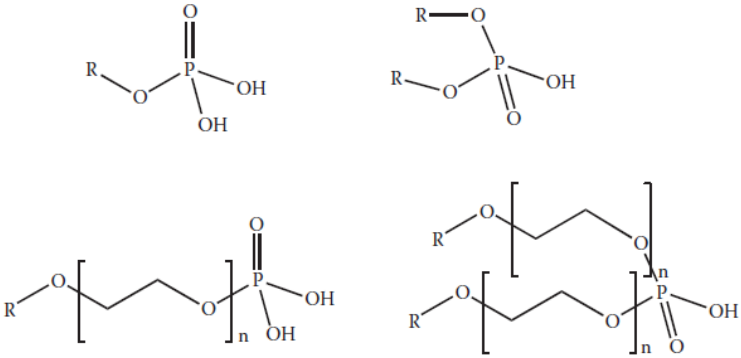
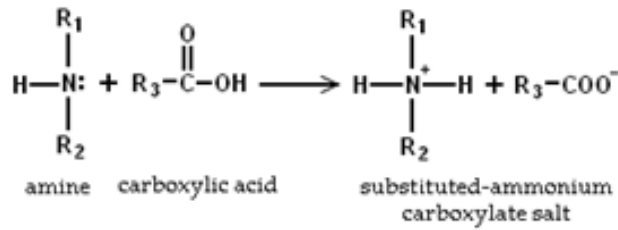
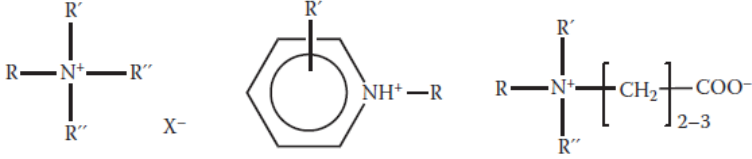
7 APPENDIX B – CORROSION INHIBITORS

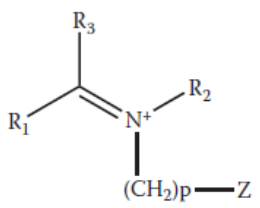
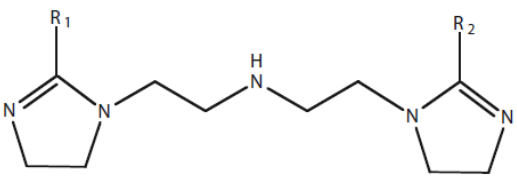
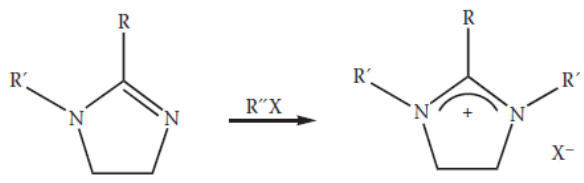
TABLE 12 - MAIN TYPES OF CORROSION INHIBITORS

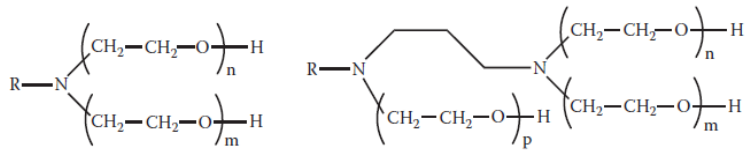
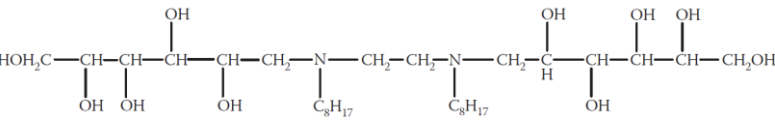
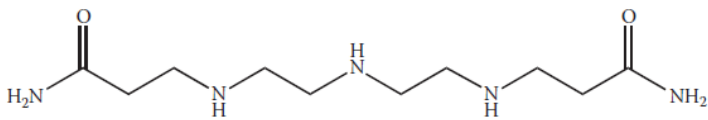
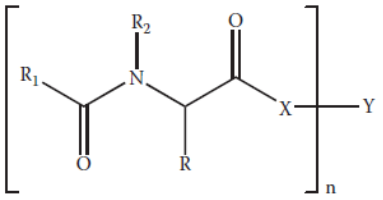
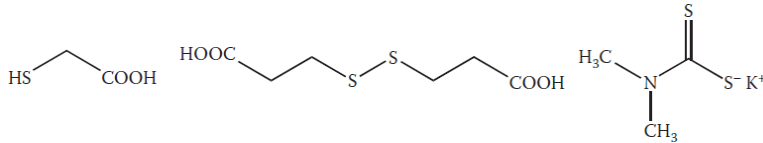
№	Type	Chemicals	Purpose and effect	Features
1	Passivating	<p>Inhibitors working in the presence of oxygen:</p> <ul style="list-style-type: none"> • Phosphate (PO_4^{3-}) and polyphosphates • Tungstate (WO_4^{2-}) • Silicate (SiO_3^{2-}) <p>Inhibitors that do not need the presence of oxygen:</p> <ul style="list-style-type: none"> • Chromate (CrO_4^-) • Nitrite (NO_2^-) • Molybdate (MoO_4^{2-}) • Meta-, ortho-, and pyrovanadates (NaVO_3, NaVO_4, and $\text{Na}_4\text{V}_2\text{O}_7$, respectively) 	Form a non-reactive thin surface on the metal that prevents access of corrosive substances to the metal surface, inhibiting further corrosion.	<p>They are not generally used for oil and gas production operations. Shows best performance in low-salinity applications; if underdosed may accelerate corrosion.</p> <p>Phosphate and polyphosphates corrosion inhibitors (CI) are nontoxic, but have limited solubility.</p> <p>Chromate CIs are carcinogenic. Molybdate CI can work both in anaerobic and even better at aerobic conditions.</p> <p>Vanadates CIs in blends with organic salts perform also as an H₂S corrosion inhibitor.</p>
2	Cathodic	Zn^{2+} ions in zinc oxide	Selectively deposits at cathodic areas increasing surface impedance. It also limits the diffusion of reducible components to these areas therefore inhibiting the reduction of water to hydrogen gas.	Are not used in oil and gas production operations but have been used in drilling fluids.

3	Vapor-phase or volatile (VpCI)	<p>Most common used VpCI:</p> <ul style="list-style-type: none"> • Dicyclohexylamine nitrite • Dicyclohexylamine carbonate • Diethylamine phosphate • Small volatile amines (triethylamine) • Benzotriazole 	<p>VpCI are organic components that can travel to the surface of the metal by gas diffusion and physically adsorbing onto the surface, because they have sufficient vapor pressure under ambient atmospheric conditions.</p>	<p>VpCI becomes polarized in the presence of moisture and will be attracted to the metal surface by different parts of the molecule.</p> <p>The cation adsorbs to the metal and forms a protective barrier to contaminants such as oxygen, water, chlorides, and other corrosion accelerators. Corrosion cell will not form and therefore corrosion will be halted. The anion will also act as a corrosion inhibitor.</p>
4	Film-forming (FFCI)	<p>The most common of FFCI are:</p> <ul style="list-style-type: none"> • phosphate esters • Various nitrogenous compounds: <ul style="list-style-type: none"> (a) amine salts of (poly)carboxylic acids (b) quaternary ammonium salts and betaines (zwitterionics) (c) amidoamines and imidazolines (d) polyhydroxy and ethoxylated amines/amidoamines (e) amides (f) other heterocyclics • sulfur compounds often with other heteroatoms such as nitrogen 	<p>As passivating CI they form a protective layer that physically prevents access of corrosive chemicals (water, chloride ions, etc.) from penetrating to the metal surface. FFCI utilized for protection of oil, condensate and gas production pipelines against H₂S, Cl⁻ and CO₂ corrosion.</p>	<p>Oil-soluble (OS) FFCIs perform better than water-soluble FFCIs in downhole continuous injection applications due to better thermal stability.</p> <p>OS FFCIs are toxic and have high bioaccumulation potential. By varying the length of the hydrophobic tail (L), the solubility of FFCI surfactants can be change. If L < 12 then film will not form, if L > 20 film may be ripped off the walls at very high shear.</p> <p>Majority of the common FFCI surfactants have a fairly high toxicity.</p>

TABLE 13 - FILM-FORMING CORROSION INHIBITORS

№	Type	Chemicals	Features
1	Phosphate esters	 <p style="text-align: center;">Figure 7.1 - Structures of typical phosphate ester FFCIs</p>	<p>These are good FFCIs, usually applied in blends with other types of FFCIs. A mixture with different hydrophilic inhibitors can be formed and will split between hydrocarbon and water phases. FFCI containing hydrophobic nonyl-phenol group are more effective than linear or branched types.</p> <p>They form fairly insoluble iron (II) and calcium salts, which may precipitate on the pipeline walls, retarding further corrosion.</p>
2	Amine salts of (poly)carboxylic acids	 <p style="text-align: center;">Figure 7.2 - Reaction of amine salts of carboxylic acids</p>	<p>This type of FFCI in blends with surfactants can have different oil or water solubility. Amine salt FFCIs, are environment-friendly.</p>
3	Quaternary ammonium salts and betaines (zwitterionics)	 <p style="text-align: center;">Figure 7.3 - Quaternary ammonium, alkyl pyridine quaternary, and zwitterionic betaine respectively</p>	<p>Also utilized in blends with other FFCIs. Usually quite toxic, useful as biocides, which prevent biofilm formation and further corrosion. Links between the long alkyl chain and the quaternary nitrogen atom can make those CI more biodegradable (Fig 7.3).</p>

		 <p>Figure 7.4 - Zwitterionic water-soluble iminium compounds (Z-carboxylate; one of R1, R2, or R3 is a hydrophobic group)</p>	<p>Zwitterionics (Fig 7.4) such as betaines are generally less toxic than ordinary surfactants and can also perform as FFCIs.</p> <p>Quaternary derivatives of oil-soluble polyalkylene-polyamines show good CO₂ corrosion inhibition properties.</p> <p>Few ester derivatives have environmentally friendly properties. Biocide with good CI properties can be made by derivatizing metronidazole (Fig 7.5).</p>
4	Amidoamines and imidazolines	 <p>Figure 7.6 - Structure of bis-imidazolines.</p>  <p>Figure 7.7 - Protonation (R'' = H) or alkylation (R = alkyl) of imidazolines</p>	<p>Imidazolines are the most common class of FFCI used in the oil and gas industry. Certain imidazoline chemical perform well in high-pressure, high-temperature (HPHT) conditions. Their salts are more hydrophilic therefore have good corrosion inhibition properties. Short hydrophobic chain length (< C₁₂) provides no corrosion inhibition. Hydrophobic tail with C₁₈ atoms showed optimal performance, but had poorest environmental properties.</p>

5	Polyhydroxy and ethoxylated amines/amidoamines	 <p>Figure 7.8 - Ethoxylated fatty amine and diamine FFCIs. R - alkyl group or R'C(=O)</p>  <p>Figure 7.9 - N,N'-dioctyl-N,N'-bis(1-deoxyglucityl)ethylenediamine</p>	<p>Ethoxylation of fatty amines by ethylene oxide gives ethoxylated amines, which are useful FFCIs. Products of reaction become more water-soluble also providing extra sites (oxygen atoms) for adsorption to the metal surface.</p>
6	Amides	 <p>Figure 7.10 An example of a polymethylenepolyaminedipropionamide FFCI</p>  <p>Figure 7.11 - Acylated derivatives of amino acids appended to a suitable backbone Y via a link group X</p>	<p>Amide derivatives with long chains are environmentally friendly FFCIs. They are hardly formulated and adversely affect the demulsification process. Some chemicals (Figure 7.10) have low-marine toxicity and perform well as CO₂ corrosion inhibitors. Amide FFCIs chemicals based on acylated derivatives of amino acids appended to a suitable backbone have a high biodegradability.</p>
7	Sulfur compounds	 <p>Figure 7.12 - Thioglycolic acid (TGA), 3,3'-dithiodipropionic acid and potassium dimethyldithiocarbamate</p>	<p>Thiosulfate ions and mercaptocarboxylic acids have synergetic effect for nitrogenous FFCIs. Some sulfur chemicals have good performance to prevent cracking corrosion. FFCIs containing water-soluble mercaptocarboxylic acids (Figure 7.12) have low toxicity and successfully</p>

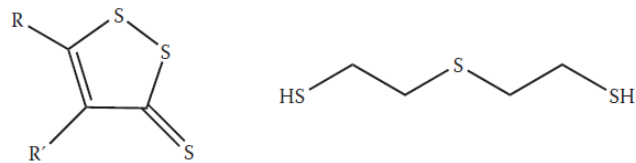


Figure 7.13 - The structure of trithiones (left) and 2-mercaptoethyl sulfide

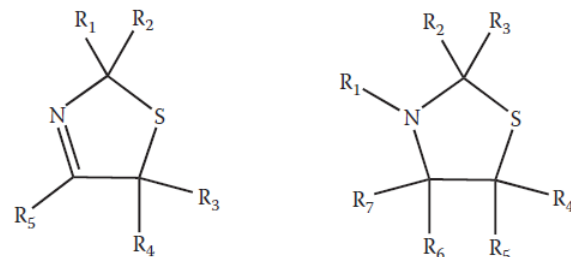


Figure 7.14 -The structure of 2,5-dihydrothiazoles and thiazolidines

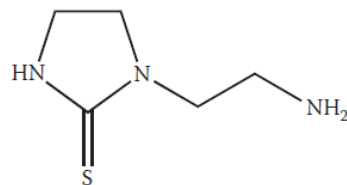


Figure 7.15 - 1-(2-aminoethyl)-2-imidazolidinethione

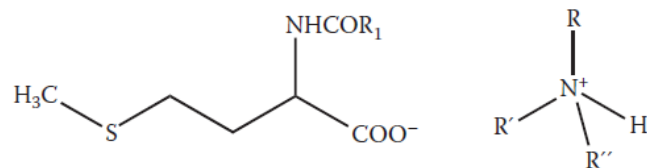


Figure 7.16 - Salts of amidomethionine derivatives and amines

utilized in high-shear stress applications. If used alone, they are less effective at inhibiting corrosion in a CO₂ environment.

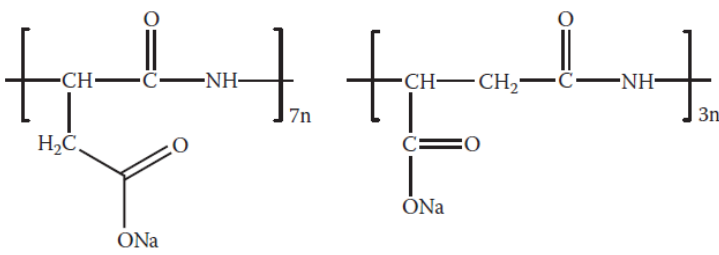
Trithiones (Figure 7.13) are chemicals containing three sulfur atoms. They are suitable dispersant and proved to be good CO₂ corrosion inhibitors in sweet wells.

Thiophosphorus chemicals have also been claimed to avoid organic acid corrosion, even this is usually a high-temperature downstream issue.

Thiocarboxylic acids have very unpleasant odors and alternatives (e.g. 2,5-Dihydrothiazoles) have been proposed. Chemicals depicted at Figure 7.14 have been claimed as VpCIs for gas well applications; even they have limited water solubility. Thiazolidines are more water-soluble.

Small nonsurfactant imidazolidinethiones (Figure 7.15) are low toxic and biodegradable FFCIs.

Salts of amidomethionine (Figure 7.16) derivatives and amines are the class of FFCI having increased biodegradability and reduced toxicity.

8	<p>Polyaminoacids and other polymeric water-soluble corrosion inhibitors</p>	 <p style="text-align: center;">Figure 7.17 - Sodium polyaspartate</p>	<p>Phosphates chemicals are used for corrosion protection in water treatment systems and also have been used as scale inhibitors. If used alone they are not effective enough for corrosion protection.</p> <p>Polyaminoacids chemicals perform very well as scale inhibitors, also having fairly good CO₂ corrosion protection. But not as good as the best FFCIs. The best known and cheapest representatives of polyaminoacids are salts of polyaspartic acid (Figure 7.17).</p> <p>This type of chemicals can be used within a corrosion- and scale-inhibitor package with added synergists to show best performance.</p>
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8 APPENDIX C – BIOCIDES

TABLE 14 - OXIDIZING BIOCIDES

№	Type	Instance chemical formula/reactions	Features
1	Electrochemically generated chlorine/ hypochlorite and bromine/hypobromite	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \text{ (anode reaction)}$ $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \text{ (catode reaction)}$ <p>Figure 8.1 - Electrolytic oxidation of the chloride ions in seawater using a DC current</p> $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$ $\text{OH}^- + \text{HOCl} \rightarrow \text{OCl}^- + \text{H}_2\text{O}$ <p>Figure 8.2 - Further reactions after electrolytic oxidation of chloride ions</p>	<p>Chlorine can be generated on site by electrolytic oxidation of the chloride ions in seawater. Then it can be utilized primarily at water-injection systems. Disadvantages of those oxidizing chemicals are that halogens compounds are toxic, corrosive, and difficult to handle. Hypochlorous acid (HOCl) is a more powerful biocide than its ions. Bromide ions presented in seawater will be also oxidized by the chlorine to bromine, which further form hypobromite (OBr⁻) ions. These ions are more powerful oxidizing biocide than hypochlorite. Generated chlorine is highly reactive and will interact with any organic species presented in the water. This will reduce material concentration available for bacterial control. Chemical is corrosive to iron in the steels and will remove bisulfite oxygen scavengers from the water, which is needed to prevent oxygen corrosion.</p>
2	Hypochlorite and hypobromite salts	$\text{MeOCl} \text{ Me}=\text{Na, K, etc.}$ $\text{MeOBr, Me}=\text{Na,K, etc.}$	<p>Utilization of these salts in seawater injection systems has following constrains: logistic, tank storage limitations and high associated transportation costs. Stable hypobromite or bromine compositions superior to hypochlorite salts have been also used.</p>
3	Stabilized bromine chloride	BrCl	<p>Bromine chloride has been made easier to handle by stabilizing it with sulfamate salts, but still has same disadvantages as the hypochlorite salts. At near-neutral pH due to hydrolysis, it effectively provides a dose of the powerful biocide hypobromous acid (HOBr). Biocidal performance can be improved by addition of C₈–C₁₄ alkylamines as synergists to these blends, meanwhile alkylamines are fairly poor nonoxidizing biocides if used alone.</p>
4	Hydroxyl radicals	$\text{OH}\cdot$	<p>Hydroxyl radicals (OH[·]) are powerful chemical for killing bacteria.</p>

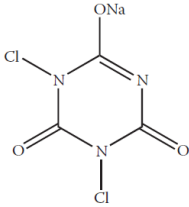
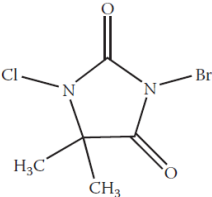
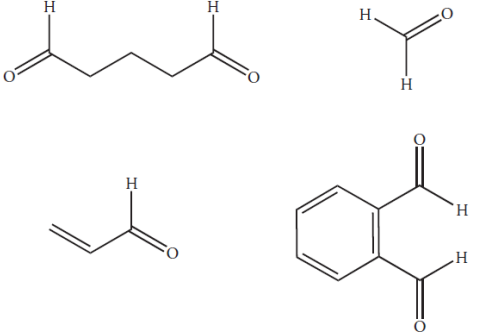
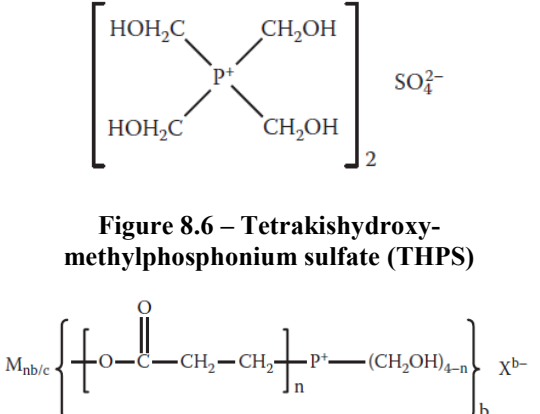
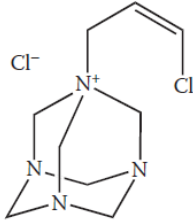
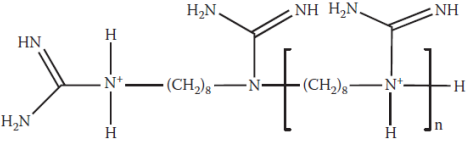
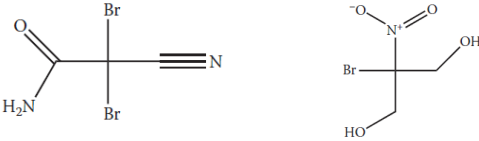
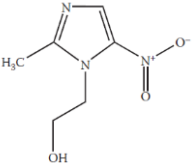
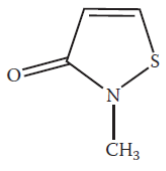
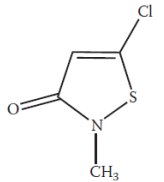

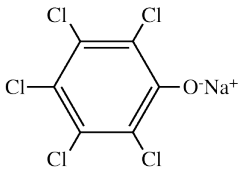
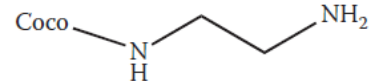
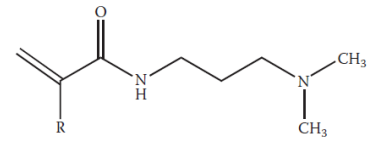
			They can be generated on-site by electrocatalytic hydroxyl radical generation and used for bacterial control. Currently not used in the oil industry.
5	Chloramines	NH_2Cl	Chloramines are superior biocides to the hypochlorites, as they contain high-valence chlorine found at N-Cl bonds. Unfortunately they are difficult to handle, however <i>in situ</i> methods have been claimed, but not yet utilized at oil industry.
6	Chlorine dioxide	ClO_2	Chlorine dioxide is usually classified as an oxidizing biocide, although its kill mechanism is not oxidation. It is an explosive gas in air but only at high concentrations. Chemical performs better at a higher pH, in nitrogen, or in organic-contaminated systems than chlorine. Its' solutions have to be stabilized to give a high active dose of chlorine dioxide. The problem has been solved by using an aqueous solution of a chlorite, a chlorine-generating agent, and a base. Chlorine dioxide solutions are corrosive.
7	Chloroisocyanurates	 <p style="text-align: center;">Figure 8.3 - Sodium dichloroisocyanuric</p>	Chloroisocyanurates are powdered solid compounds, which can be easily handled by hydrolyzing in water to slowly release chlorine and cyanuric acid. Sodium dichloroisocyanuric acid (Figure 8.3) is an example in this class. Disadvantages of this class are that they are corrosive and also suffer all the drawbacks of the other chlorine-containing products in pH effectiveness ranges.
8	Halogen-containing hydantoin	 <p style="text-align: center;">Figure 8.4 - 1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)</p>	These chemicals are solids which by reacting with water slowly releases hypochlorous and hypobromous acid. 1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) is a representative of this type of chemicals and at the same dosage is more active than sodium hypochlorite for destroying biofilms. It is also less corrosive. The hydantoin are widely used as biocides in a variety of industries.

TABLE 15 - NONOXIDIZING ORGANIC BIOCIDES

№	Type	Instance chemical formula/reactions	Features
1	Aldehydes	 <p align="center">Figure 8.5 - Glutaraldehyde (top left), formaldehyde (top right), acrolein (bottom left), and ortho-phthalaldehyde (bottom right)</p>	<p>Aldehydes are a chemical that kills SRB populations (Fig. 8.5). They are also H₂S scavengers. Glutaraldehyde is the most commonly used oilfield nonoxidizing biocide. It kills cells by cross-linking outer proteins and blocking cell permeability. Glutaraldehyde is unstable on storage and very pH-sensitive. Chemical works well at pH > 6.5 being effective for injection waters but less effective for produced water treatments. Formaldehyde is low-cost, effective in killing sessile microorganisms in established biofilms chemical. Due to its carcinogenic properties it has been banned in Europe. Acrolein is an effective biocide, also like the other small aldehydes, it scavenges H₂S, and even dissolves iron sulfide. Ortho-phthalaldehyde can remove sessile populations at lower doses with less contact time and have been proposed as an improvement of glutaraldehyde.</p>
2	Quaternary phosphonium compounds	 <p align="center">Figure 8.6 – Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)</p> <p align="center">Figure 8.7 - Reaction products of acrylic acid and tetrakis-hydroxymethylphosphonium</p>	<p>Salts of the THPS are excellent nonoxidizing, nonfoaming biocides, which are widely used in the oil and gas industry. These chemicals kill bacteria in different ways, but generally by cross-linking of proteins, which collapses cell membranes. It is environmentally friendly chemical, as it loses antimicrobial properties by degrading to a nontoxic substance immediately after being discharged to the sea. THPS can cause corrosion under specific conditions, but in other cases it is an effective inhibitor. They also react or interfere with the performance of commonly used O₂ scavengers, resulting in not complete deaeration of systems. If injected with an ammonium salt, THPS can also remove iron sulfide scale both downhole and topside. The iron becomes chelated to a nitrogen-phosphorus ligand, making the water have a red color. FeS removal from produced fluids also improves demulsification processes. Reaction products of acrylic acid and THPS salts (Fig. 8.7) perform well as biocides and also dissolve iron sulfide, but not currently commercially available.</p>

3	Quaternary ammonium surfactants	 <p>Figure 8.8 - 1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane</p>	<p>These biocides are very surface-active and because of this sometimes utilized in blends with other biocides to improve the performance. They are generally most effective against algae and bacteria in pH ranges > 8, but lose their activity in systems with dirt, oil, and other debris.</p> <p>Due to the cationic nature electrostatic bond is formed with the cell wall, which prevents permeability and thereby protein starts denaturing. If used alone, quaternary ammonium surfactants biocides can take up to 10 min to kill bacteria. Because of its surfactant properties they perform as a film-forming corrosion inhibitors. These chemicals are often led to foaming, but nonfoaming biocidal surfactants have been discovered.</p>
4	Cationic polymers	 <p>Figure 8.9 - Poly(hexamethylene)biguanide hydrochloride (n = 1-3)</p>	<p>Cationic polymers are good biodegradable corrosion inhibitors and biocides. Biguanides is the class of cationic polymeric biocides as for example, poly-(hexamethylene)biguanide hydrochloride (Figure 8.9). These chemicals are very short polymers or oligomers and have been mainly used as disinfectants.</p>
5	Organic bromides	 <p>Figure 8.10-2,2-dibromo-3-nitropropionamide (DBNPA) Figure 8.11 - 2-Bromo-2-nitropropanediol (BNPD)</p>	<p>Organic bromides have been used as a biocide in oilfield operations. BNPD (Fig 8.11) was invented in the sixties and is quite well known chemical. DBNPA is pH-sensitive chemical which quickly hydrolyze under both acid and alkaline conditions (Fig 8.10). For this property it is even preferred as it quickly kills bacteria and then quickly degrades to ammonia and bromide ions. DBNPA can act synergistically with a number of oxidizing and nonoxidizing biocides.</p>
6	Metronidazole	 <p>Figure 8.12 - Metronidazole</p>	<p>Metronidazole is a biocide with weak corrosion-inhibiting properties (Fig 8.12). It is selectively absorbs by anaerobic bacteria. The nitro group of metronidazole is chemically reduced by ferredoxin and reaction products disrupt the DNA helical structure. It has been effectively performed in controlling biogenic sulfide production at water injection systems.</p>

7	Isothiazolones and thiones	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Figure 8.14 - 2-methyl-4-isothiazolin-3-one</p> </div> <div style="text-align: center;">  <p>Figure 8.13 - Chloro-2-methyl-4-isothiazolin-3-one</p> </div> </div>	<p>These chemicals are biocides with good biodegradability, effective against biofilms. Isothiazolones inhibit microbial respiration and food transport through the cell wall leading to the death of the cell. Unfortunately SRB can produce hydrogen sulfide which will reduce the effectiveness of isothiazolones, even if they are used as biocides. This type of chemicals is however effective biostat maintaining a low level of SRB and inhibiting their metabolic activity. Low level of SRB prevents the formation of hydrogen sulfide; that is why they are best used in combination with other organic biocides.</p>
8	Organic thiocyanates	<div style="text-align: center;">  <p>Figure 8.15 - Methylene bis(thiocyanate)</p> </div>	<p>Only one chemical from this class has been widely used (Fig. 8.15). It kills bacteria by blocking the transfer of electrons in the microorganism, avoiding oxidation and reduction processes. It has following disadvantages: (a) rapid decomposes above at pH > 8.0 and releases toxic hydrogen cyanide; (b) relatively expensive; (c) needs a dispersant to obtain effective penetration of the biocide into the biofouling; (d) requires fairly high concentrations.</p>
9	Phenolics	<div style="text-align: center;">  <p>Figure 8.16 - Sodium pentachlorophenate</p> </div>	<p>Phenolics are low-cost and powerful type of biocide chemicals. Because of environmental concerns this class has been withdrawn from most markets.</p>
10	Alkylamines, diamines, and triamines	<div style="display: flex; flex-direction: column; align-items: center;"> <div style="text-align: center;">  <p>Figure 8.17 - Cocodiamine</p> </div> <div style="text-align: center;">  <p>Figure 8.18 - Dimethylaminopropylmethacrylamide (R = CH3)</p> </div> </div>	<p>Alkylamines have long been used as a biocide in the oil industry (e.g. cocodiamine - Figure 8.17). Nonsurfactant chemicals - tertiary amine acrylamide monomers, have been shown to inhibit microbiological growth (Fig. 8.18). In the presence of corrosion inhibitors they will not only improve corrosion performance, but also kill 100% of bacteria even if present in lesser amounts than are required when corrosion inhibitor is not present.</p>

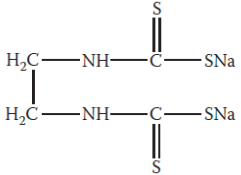

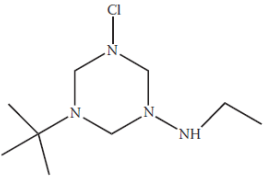
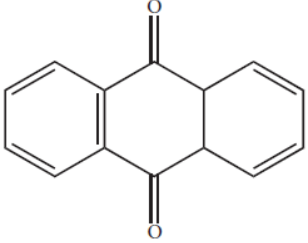
11	Dithiocarbama tes	 <p style="text-align: center;">Figure 8.19 - Disodium ethylene-1,2-bisdithiocarbamate</p>	Generally used more in the paper industry, sometimes in blends with aldehydes.
12	2-(decylthio) ethanamine (DTEA) and its hydrochloride	 <p style="text-align: center;">Figure 8.20 - 2-(Decylthio)ethanamine hydrochloride (DTEA)</p>	Amine and the hydrochloride chemicals have biocidal properties. The hydrochloride is a quaternary surfactant and has been shown to have additional corrosion inhibition properties. DTEA (Figure 8.20) present at low pH as the hydrochloride and at high pH as the free amine.
13	Triazine derivatives	 <p style="text-align: center;">Figure 8.21 - 2-(tert-Butylamino)-4-chloro-6-(ethylamino)-S-triazine.</p>	Certain triazine chemicals have bactericidal properties. Some triazine derivatives that are used as H ₂ S scavengers are also commercially available as biocides.

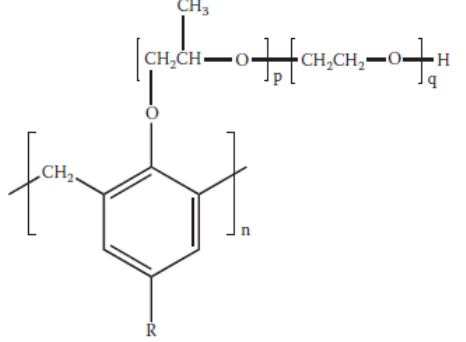
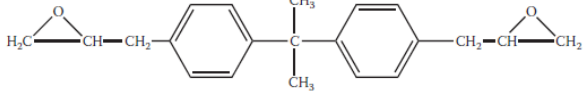
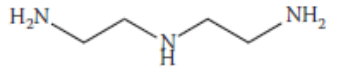
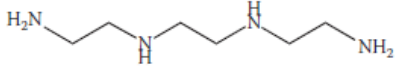
TABLE 16 - BIOSTATS

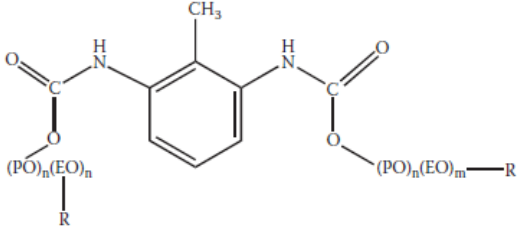
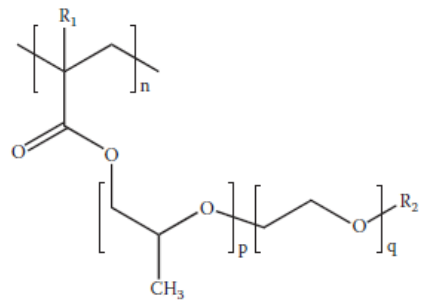
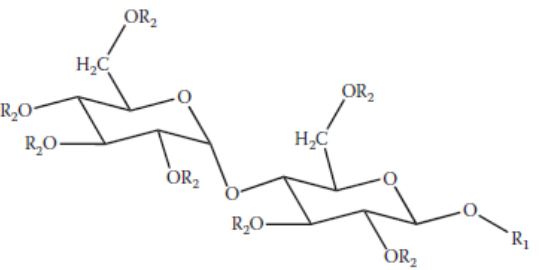
№	Type	Instance chemical formula/reactions	Features
1	Anthraquinone	 <p data-bbox="528 571 864 600">Figure 8.22 – Anthraquinone</p>	<p>Anthraquinone is oil-soluble biostat, meanwhile its salt (9,10-anthracenediol disodium) is a water-soluble compound and works as if it were anthraquinone. These chemicals inhibit sulfate respiration of SRBs having little effect on other classes of bacteria. It has been used as a biostat in a number of projects since the late nineties.</p>
2	Nitrite and nitrate ions	<p>Nitrite (NO_2^-) and nitrate ions (NO_3^-)</p>	<p>These chemicals are found in calcium or sodium nitrate/nitrite salts. They are cheap, easy to handle, environment-friendly inorganic chemical becoming more and more used in the oil industry to inhibit SRB.</p> <p>Nitrite is reduced more slowly than sulfite directly inhibiting sulfate reduction by SRB. Addition of nitrite ions to produced or injection water systems can control sulfide formation if present in high-enough concentration. It mainly depends on pH, nitrite ions reaction with H_2S to form sulfur and reduced nitrogen compounds.</p> <p>Ca or Na nitrate are environmental friendly SRB biostats selectively stimulating and increasing the targeted nitrate-reducing bacteria. Utilization of molybdenum compound may improve the treatment effect. This element is a known as enzymatic inhibitor of the hydrogenase enzyme found in SRB. If nitrate and nitrite salts are injected very late in the system, treatment may not totally eliminate the application of biocides.</p> <p>Microbial-enhanced oil recovery (MEOR) is a potentially large advantageous side effect of using nitrate-based water injection treatments. NR-SOB biofilms will be formed in the reservoir and will lead to releasing more oil the reservoir rock, increasing recovery factor.</p>

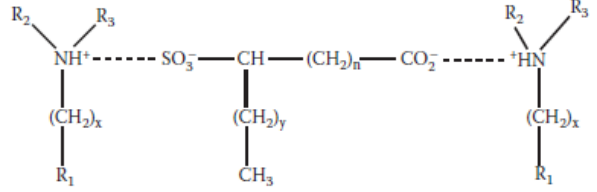
3	Azide salts	NaN ₃	Sodium azide is a well-known biostat and has been used for preventing biofouling of wells. It inhibits cytochrome oxidase in gram-negative bacteria. Effect of this chemical on SRB is not yet investigated.
4	Other biostats	SeO ₄ ²⁻ , VO ₄ ³⁻ , MoO ₄ ²⁻ , MnO ₄ ⁻ , WO ₄ ²⁻	Other biostat inhibiting SRB growth are usually more expensive. They include selenate, vanadate, molybdate, permanganate, and tungstate ions. Molybdate ions can be also used in some corrosion inhibitor blends. The metal oxide anion SRB inhibitors are used to deplete ATP pools in the SRB, thereby, resulting in the death of the SRB.

9 APPENDIX D – EMULSION BREAKERS

TABLE 17 - DEMULSIFIERS

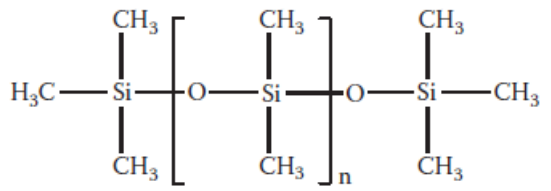
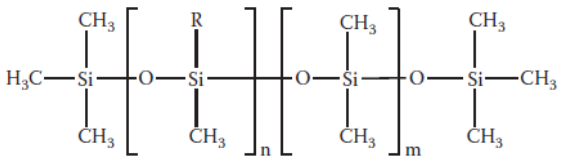
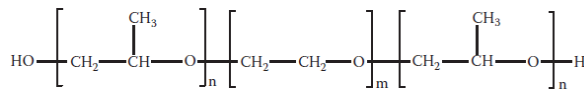
№	Type	Instance chemical formula/reactions	Features
1	Alkylphenol-Aldehyde Resin Alkoxyates	 <p>Figure 9.1 - Alkylphenol-aldehyde resin alkoxyates</p>	<p>Most common class of demulsifier. It has very consistent high performance and ease of manufacture. Varying the length of alkyl groups on the phenol ring can vary the hydrophobicity of molecule. Molecular weights these resin are in the range of 5,000–50,000 Da.</p> <p>Alkylphenols formed by degradation of ethoxylated alkylphenols, are known to be endocrine disrupters in marine species. These molecules are present in trace quantities as unreacted monomers in the finished demulsifier. They can be also formed as degradation products after discharge of the water. Alkylphenol-aldehyde resin alkoxyates (Figure 9.1) are almost oil-soluble and have low human toxicity.</p>
2	Polyalkoxylates of Polyols or Glycidyl Ethers	 <p>Figure 9.2 - Bis-phenol A, a diglycidyl ether</p>	<p>As branched polyalkoxylates is than higher is the demulsifier efficiency. To increase the molecular weight polyalkoxylates of polyols (Figure 9.2) can be partially cross-linked with a vinyl monomer such as acrylic acid and thus improve demulsifier efficiency.</p>
3	Polyamine Polyalkoxylates and Related Cationic Polymers	 <p>Figure 9.3 - DETA</p>  <p>Figure 9.4 - TETA</p>	<p>Small polyalkyleneamines chemicals are commercially available and can form a reaction with various amounts of ethylene oxide and propylene oxide to produce branched demulsifiers (Figure 9.3-9.4).</p> <p>Some products of this type of chemicals have an excellent breaking effect even at a very low concentration.</p>

4	Polyurethanes (Carbamates) and Polyalkoxylate Derivatives	 <p style="text-align: center;">Figure 9.5 - Polyurethane polyalkoxylate (dicarbamate)</p>	Well-known class of demulsifier. Acts synergistically with previous type of chemicals when added simultaneously. They significantly increase water separation rates than if used individually. They “bridge” nearby water droplets in moderate concentrations, but retards water coalescence if added at significantly higher concentrations.
5	Vinyl Polymers	 <p style="text-align: center;">Figure 9.6 - Alkyl polyalkoxylate (meth)acrylate ester polymers. R1 = H or CH3, R2 = H or alkyl</p>	A wide variety of these chemicals have been used as demulsifiers. They contain both hydrophilic and hydrophobic parts in their structure. Superior demulsifiers that give rapid water separation, zero residual emulsion, and sharp oil-water interface, clear water phase for disposal or reinjection and low salt in crude content can be produced by introducing hydrophobic groups by using monomers.
6	Biodegradable Demulsifier	 <p style="text-align: center;">Figure 9.7- Example of an alkyl polyglycoside based on a β-maltose backbone</p>	Alkoxylated alkyl polyglycosides (Figure 9.7) is another class of potentially biodegradable demulsifiers. To increase performance these chemical can be the branched leading to higher molecular weight.

7	Dual-Purpose Demulsifiers	 <p>Figure 9.8 - Three-tailed ion pair demulsifiers</p>	<p>Dualism of some demulsifiers can be expressed in a secondary chemical function. Salt of an alkyl amine and an alkyl aryl sulfonic acid is a useful demulsifier but also has corrosion-inhibiting properties; specific example of that salt is methyl, dicocoyl amine, and an alkyl aryl sulfonic acid (Figure 9.8) which probably exists as ion pairs in nonpolar solvents.</p> <p>Some chemicals were designed for other purposes, but showed good demulsifying effect. For example, sulfonic acid derivatives of alkyl aromatic compounds containing at least two 6-rings and an alkyl chain of at least C₁₆ were first designed as asphaltene inhibitors. These molecules together with a solvent also behave as demulsifiers probably by stabilizing the asphaltene, which are known to cause emulsion problems.</p>
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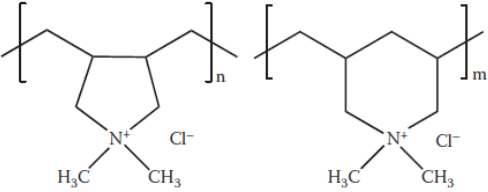
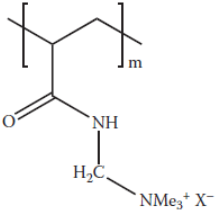
10 APPENDIX E – DEFOAMERS AND ANTIFOAMS

TABLE 18 - TYPICAL DEFOAMERS AND ANTIFOAM

№	Type	Instance chemical formula/reactions	Features
1	Silicones	 <p>Figure 10.1 - Structure of poly(dimethylsiloxane) (PDMS)</p>	<p>This type of chemicals is the most commonly used antifoams for oilfield operations. Unfortunately siloxane polymers are poorly biodegradable, but at the same time nontoxic chemicals. They can be utilized as pure compound or with solvents or in emulsion form.</p> <p>One of the simplest and common reagents used in industry is PDMS (Figure 10.1). It is polymer with molecular weight ranging from 15,000 up to 130,000 Da. It was proposed to work best as antifoam for crude oil applications. Silicones if overdosed can cause potential damage to the catalysts at the refinery.</p>
2	Fluorosilicones	 <p>$R = C_nF_{2n+1}$ or $CF_3CH_2CH_2$</p> <p>Figure 10.2 - Fluorosilicone chemical</p>	<p>Other class of antifoams is modified silicon by substituted fluorinated alkyl groups, which improve antifoam performance making these chemicals even less soluble in hydrocarbons. They are more expensive than silicones, but they usually require lower doses.</p> <p>Co-utilization of these chemicals with nonfluorinated silicones gives synergistic effect. Blend performs at a lower dose better providing reduced liquid carry over into a gas stream and reduced gas carry under into a liquid stream either than applying silicones (PDMS) alone.</p>
3	Polyglycols	 <p>Figure 10.3 - A linear diblock ethylene oxide / propylene oxide copolymer: n > m for defoamers.</p>	<p>These chemicals are good defoamers, which remove foams at aqueous solutions but can be also used for crude oil separators or glycol systems. Disadvantage of those chemicals - relatively high dose requirement (10-200 ppm). If overdosed may cause the reason for stabilizing foams and leading to control loss in the separator/glycol system.</p> <p>They are much more biodegradable and will not damage refinery catalyst. As well as silicones they are low in toxicity.</p>

11 APPENDIX F – FLOCCULATION CHEMICALS

TABLE 19 - FLOCCULANTS FOR OIL AND GAS INDUSTRY

№	Type	Instance chemical formula	Features
1	Highly valent metal salts	Iron (III), zinc (II), or aluminum (III) salts are the most common.	<p>Due to a high positive charge density these chemicals have flocculation or coagulant properties. Usually used as additives to improve polymer flocculants efficiency in oilfield operations. They hydrolyze in aqueous environment forming acidic solution which can lead to corrosion issues. Their hydroxides - products of hydrolysis, can form flocs and unnecessary sludge in solution. Some metal ions are restricted to be discharged in some regions. H_3O^+ ion generating acids break oily water better than coagulant salts. Unfortunately acidic wastewater is corrosive and should be neutralized after separation stage.</p>
2	Cationic polymers	<div style="text-align: center;">  <p>Figure 11.1 - DADMAC polymers</p>  <p>Figure 11.2 - The active monomer structure in acrylamide Mannich copolymers</p> </div>	<p>These chemicals are most used in oil and gas industry. Oil particles dispersed in water usually have negative charge, which makes these chemicals preferable for usage. Polymer performance can be improved if its monomers are polymerized in polyvalent anionic salt solution.</p> <p>These reagents are made cationic due to presence of quaternary nitrogen atoms usually inside five- or six- rings monomers. First monomer is the major component and the six-ring monomer is the minor component at basic cationic DADMAC polymers (Fig. 11.1). DADMAC polymers have been known as a good flocculants for a long time.</p> <p>Effective performance of those polymers depends on its charge density, which can be varied by copolymerization of DADMAC monomers with acrylamide (Fig. 11.3, n = 2, 3) or other cheap, nonionic monomeric hydrophilic monomers. If these polymers are modified as they become hydrophobic, it might improve flocculant</p>

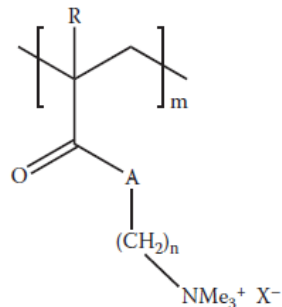


Figure 11.3 - Structure of acrylamide or acrylate-based moneric units (A - NH/O, R- H/CH3)

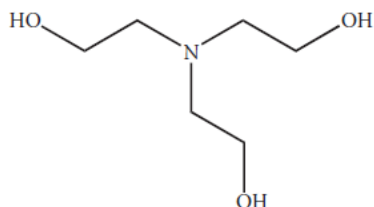


Figure 11.4 - The structure of triethanolamine

performance, as polymer hydrophobic parts will be attracted to hydrophobic oil particles, enhancing their flocculation.

Well-known cationic flocculants are Mannich acrylamide polymers (Fig.11.2) greatly performing in the form of inverse microemulsions. As DADMAC polymers their cation density can be varied by copolymerization with neutral hydrophilic monomers such as cheap acrylamide, therefore enhancing flocculant effectiveness. These polymers have very low bulk viscosity and can be prepared even at high solids content.

Molecules containing peripheral OH groups and nitrogen atom, such as diethanolamine, triethanolamines (Fig 11.4), and isopropanolamines are cheap materials, which can form branched polyalkanolamines. Resulting cationic polymers are useful as oily water demulsifiers.

3 Anionic polymers

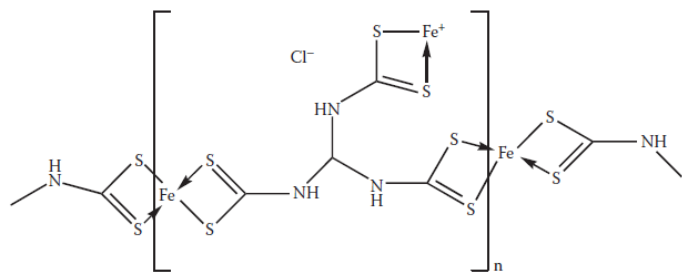
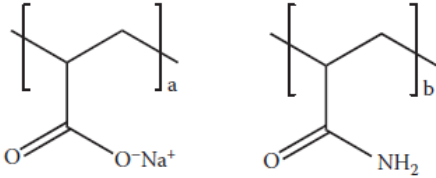
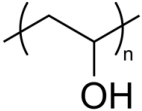


Figure 11.5 - A simple DTC, cross-linked and cationized with ferrous ion

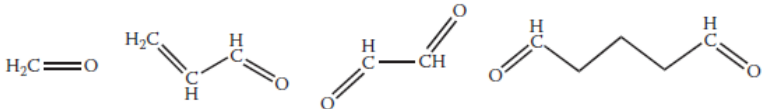
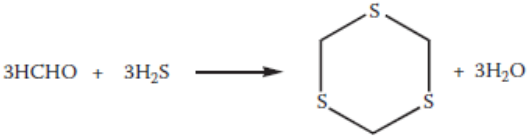
Works for particles and oily droplets with positive surface charge. These chemicals have some advantages over the high molecular weight cationic polymers as they have low molecular weight and are soluble in water anionic polymers. One of the common representative of this type is the DTCs (Fig 11.5). It has an interesting feature as it can form a high molecular weight cationic *in situ* by forming complexes with iron (II) ions. They can be applied at fairly high concentrations without being too viscous, because injected anionic polymers have low molecular weight.

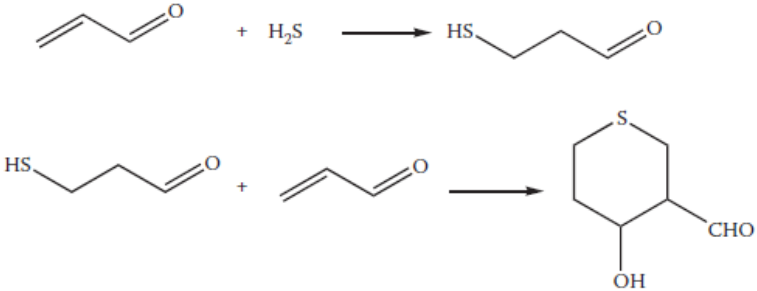
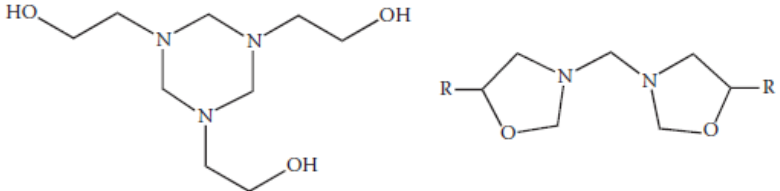
High molecular weight acrylic polymer salts (Fig 11.6 - two monomer groups often found in commercial anionic flocculants) are dominating at the market. Partially hydrolyzed polyacrylamide can be utilized alternatively. If pure nonionic is required for usage,

		 <p data-bbox="483 395 1081 422">Figure 11.6 - Sodium acrylate/acrylamide copolymer</p>	<p data-bbox="1211 140 1794 167">unhydrolyzed polyacrylamide can be applied.</p>
4	Nonionic polymers	 <p data-bbox="568 624 996 651">Figure 11.7 - Polyvinyl alcohol (PVA)</p>	<p data-bbox="1211 448 2101 520">These chemicals have been investigated but are generally poorer flocculants than cationic or anionic polymers.</p> <p data-bbox="1211 531 2101 603">Polyvinyl alcohol is one of the representatives of this type of reagents.</p>

12 APPENDIX G – H₂S SCAVENGERS

TABLE 20 - H₂S SCAVENGE CHEMICALS

№	Type	Instance chemical formula	Features
1	Solid scavengers	ZnO, FeO and other zinc- or iron- based material	Due to solid state these chemicals are only applicable for sour gas treatment in process facilities.
2	Oxidizing chemicals	NaClO ₂ , NaBrO ₃ , NaNO ₂ and persalts	<p>H₂S can be scavenged by oxidizing reaction. Chlorite chemicals can react very rapidly with hydrogen sulfide. Their applications are restricted, as they provide sulfur deposition and corrosion problems leading to handling and operational problems.</p> <p>Solution of sodium nitrite can be used for sour oil and gas wells being squeezed downhole. Field experience has proved those solutions efficient removal of H₂S from the aqueous and gas phases. At other side this method also reduces corrosion issue due to H₂S and FeS scale removal from the near-wellbore area.</p>
3	Aldehydes	<div style="text-align: center;">  <p>Figure 12.1 - Formaldehyde, acrolein, glyoxal, and glutaraldehyde</p> </div> <div style="text-align: center;">  <p>Figure 12.2 - Reaction of formaldehyde with H₂S</p> </div>	<p>Aldehydes can be used as H₂S scavenge chemicals presented at Figure 12.1. Formaldehydes reacts with hydrogen sulfide forming mainly the ring compound 1,2,3-trithiane (Figure 12.2). Unfortunately it is banned in Europe due to its carcinogenic feature, and therefore not much used today.</p> <p>These chemicals have different partition fractions within water and hydrocarbon phase. As larger the aldehyde greater fraction will be dissolved into the liquid hydrocarbon phase. Small aldehydes as formaldehyde, glyoxal and glutaraldehyde will be preferably come into the brine phase (98–99%). Meanwhile over half of acrolein dissolves into the liquid hydrocarbon phase. This chemical (acrolein) has proved to be very effective sulfides scavenger. It has high toxicity and lead to handling problems that is why it is not widely used.</p> <p>Reaction products of H₂S scavenging are poorly soluble in water,</p>

		 <p style="text-align: center;">Figure 12.3 - Reaction of acrolein with H₂S</p>	<p>which can be unfavorable in some cases.</p> <p>One advantage of those chemicals is that they have the additional impact as biocides. Aldehydes can kill SRBs controlling their formation, preventing and removing formation of hydrogen sulfide even any quantities of H₂S are still formed what makes them suitable for water injection projects, as well as near-wellbore or downhole squeeze treatments. For example, acrolein can act as hydrogen sulfide scavenger, as well as biocide, and finally it also dissolves FeS scale. H₂S scavenging reaction by acrolein is shown at Figure 12.3; final product thiopyran is water-soluble product.</p>
4	Triazines	 <p style="text-align: center;">Figure 12.4 - Product of formaldehyde and ethanolamine (left) and N,N'-methylenebis-oxazolidinones (right). R = alkyl.</p>	<p>This type of chemicals consists from water-soluble compounds made by reaction between previous class representative – formaldehyde and alkanolamines. Product of formaldehyde reaction with ethanolamine is 1,3,5-tri-(2-hydroxyethyl)-hexahydro-S-triazine (Figure 12.4). These chemicals react faster with hydrogen sulfide than aldehydes, have low toxicity and usually are biodegradable. Its mixtures can contain small amounts of free formaldehyde, which is carcinogen. Triazine liquid scavengers can be regenerated by hot aqueous treatment and are economical up to about 50 kg of H₂S/day. H₂S concentrations in final product in streams with relatively low concentrations of H₂S will not exceed approximately 5-ppm. Triazines are usually injected as aqueous or methanol/water solutions.</p> <p>One disadvantage related to the triazines is that they contain tertiary amine which raises the pH of the water. Reaction products (amines) of the triazine with hydrogen sulfide are also basic in water solution. The increase in pH can lead to new or increased CaCO₃ scaling issues. H₂S-scavenging aldehyde can be used in this case which is not basic, or treat with additional carbonate scale inhibitor.</p>

5	Carboxylated metals and chelates	$\text{Zn(OOCR)}_2 + \text{H}_2\text{S} \leftrightarrow \text{ZnS} + 2\text{HOOCR}$ <p>Figure 12.5 - Zn carboxylate reaction with H2S</p>	<p>High-valence metal chelates which can be water- or oil- soluble have been used to scavenge H₂S from operational streams. These chemicals have been used for drilling fluids, contaminated waste water and oil production streams.</p> <p>Zinc(II) or iron(III) are the common metals presented at this type of scavenges. Carboxylated groups are found at chelate which can be based on different acids or even become more biodegradable if gluconate chelate is utilized.</p> <p>Carboxylated metals (zinc and iron) are oil-soluble H₂S scavengers. They were effectively applied in some projects, for example, for treating a 1,200-ppm hydrogen sulfide–contaminated oil stream. Carboxylates react with hydrogen sulfide forming ZnS, which becomes transportable dispersion in the oil phase (Figure 12.5).</p>
6	Other amine-based products	RC(=NH)NH_2	<p>Water-soluble amidines are small chemicals which can be present also in oligomeric formulations have good hydrogen sulfide scavenger properties.</p>

13 APPENDIX H – “EMPTY TO ZERO” GAWK PROGRAM

```
BEGIN {
    FS = "\t"
    foundDATA = 0;
    foundCol = 0;
}

/^DATA/ {foundDATA = 1;}

foundDATA && !foundCol {
    for (i=1; i<=NF; ++i) {
        if ($i == colname) {
            colNumber = i;
            foundCol = 1;
        }
    }
}

foundCol {
    if ($colNumber == "") {
        $colNumber = "0";
    }
}

{
    for (i=1; i<=NF-1; ++i) {
        printf("%s\t", $i);
    }
    if (NF>=1) {
        printf("%s\n", $NF);
    }
}

# Usage:
#
# gawk -f empty2zero.awk -v colname="COLNAME" < input.str
#
# From Pipe-It script:
#
# cmd /c "gawk -f empty2zero.awk -v colname="COLNAME" < input.str >
# outputfile.str"
#
# where COLNAME must be substituted with the column that you want
# to be processed, and input.str is substituted with the
# data file in streamz format.
#
# FS = "\t" is necessary to avoid that it skips consecutive tabs
# It searches first for DATA at the beginning of the line. Then
# it searches for the column number of the heading given on the
# command line. When the column number has been found, it
# inserts 0 if there was nothing in that column on each row.
# (Printing is split in two blocks to avoid an extra tab at the end
# of the line.)
# 2013-04-02 Gunnar Borthne
```

14 APPENDIX I – “ZERO TO PREVIOUS” GAWK PROGRAM

```
BEGIN {
    FS = "\t"
    foundDATA = 0;
    foundCol = 0;
    prevValue = 0;
    HeaderLineNR = 0;
}

/^DATA/ {foundDATA = 1;}

foundDATA && !foundCol {
    for (i=1; i<=NF; ++i) {
        if ($i == colname) {
            colNumber = i;
            foundCol = 1;
            HeaderLineNR = NR;
        }
    }
}

foundCol {
    if ($colNumber == "0" && NR > HeaderLineNR+1) {
        $colNumber = prevValue;
    } else {
        prevValue = $colNumber;
    }
}

{
    for (i=1; i<=NF-1; ++i) {
        printf("%s\t", $i);
    }
    if (NF>=1) {
        printf("%s\n", $NF);
    }
}

# Usage:
# gawk -f zero2prev.awk -v colname="COLNAME" < input.str
# From Pipe-It script:
# cmd /c "gawk -f zero2prev.awk -v colname="COLNAME" < input.str >
# outputfile.str"
# where COLNAME must be substituted with the column that you want
# to be processed, and input.str is substituted with the
# data file in streamz format.
# FS = "\t" is necessary to avoid that it skips consecutive tabs
# It searches first for DATA at the beginning of the line. Then
# it searches for the column number of the heading given on the
# command line. When the column number has been found, it
# inserts in each line and specified column the value from the previous line if
# the original value was 0.
# (Printing is split in two blocks to avoid an extra tab at the end
# of the line.)
# 2013-04-02 Gunnar Borthne
```

15 APPENDIX J – BaSO_4 SATURATION INDEX CALCULATION – HEADER LEVEL (STREXZEL MACRO)

```
// Macro version 1.0
INSERT VARIABLE Ca_Ions_Water2 AFTER Ba_precip_M real
INSERT VARIABLE Ca_Ions_Water AFTER Ca_Ions_Water2 real
SET FORMULA Ca_Ions_Water2 = Ca*"Water_Rate_STB/day"
INSERT VARIABLE WatRate_cum BEFORE Ca_Ions_Water2 real
SET FORMULA WatRate_cum = "Water_Rate_STB/day"
ACCUMULATE WatRate_cum ascending

INSERT VARIABLE Wellhead_Temperature_deg_F_cum2 AFTER WatRate_cum real
INSERT VARIABLE Wellhead_Temperature_deg_F_cum AFTER Wellhead_Temperature_deg_F_cum2 real
SET FORMULA Wellhead_Temperature_deg_F_cum2 =
Wellhead_Temperature_deg_F*"Water_Rate_STB/day"
ACCUMULATE Wellhead_Temperature_deg_F_cum2 ascending
SET FORMULA Wellhead_Temperature_deg_F_cum = Wellhead_Temperature_deg_F_cum2/WatRate_cum
INSERT VARIABLE Wellhead_Pressure_psia_cum AFTER Wellhead_Temperature_deg_F_cum2 real
SET FORMULA Wellhead_Pressure_psia_cum = 319
REMOVE VARIABLE NAMED Wellhead_Temperature_deg_F_cum2

SET FORMULA Ca_Ions_Water = Ca_Ions_Water2
ACCUMULATE Ca_Ions_Water ascending
REMOVE VARIABLE Ca_Ions_Water2
INSERT VARIABLE Ca_cum AFTER Ca_Ions_Water real
SET FORMULA Ca_cum = Ca_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Ca_Ions_Water

INSERT VARIABLE Sr_Ions_Water2 AFTER Ca_cum real
INSERT VARIABLE Sr_Ions_Water AFTER Sr_Ions_Water2 real
SET FORMULA Sr_Ions_Water2 = Sr*"Water_Rate_STB/day"
SET FORMULA Sr_Ions_Water = Sr_Ions_Water2
ACCUMULATE Sr_Ions_Water ascending
REMOVE VARIABLE Sr_Ions_Water2
INSERT VARIABLE Sr_cum AFTER Sr_Ions_Water real
SET FORMULA Sr_cum = Sr_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Sr_Ions_Water

INSERT VARIABLE Ba_Ions_Water2 AFTER Sr_cum real
INSERT VARIABLE Ba_Ions_Water AFTER Ba_Ions_Water2 real
SET FORMULA Ba_Ions_Water2 = Ba*"Water_Rate_STB/day"
SET FORMULA Ba_Ions_Water = Ba_Ions_Water2
ACCUMULATE Ba_Ions_Water ascending
REMOVE VARIABLE Ba_Ions_Water2
INSERT VARIABLE Ba_cum AFTER Ba_Ions_Water real
SET FORMULA Ba_cum = Ba_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Ba_Ions_Water

INSERT VARIABLE SO4_icp_Ions_Water2 AFTER Ba_cum real
INSERT VARIABLE SO4_icp_Ions_Water AFTER SO4_icp_Ions_Water2 real
SET FORMULA SO4_icp_Ions_Water2 = SO4_icp*"Water_Rate_STB/day"
SET FORMULA SO4_icp_Ions_Water = SO4_icp_Ions_Water2
ACCUMULATE SO4_icp_Ions_Water ascending
REMOVE VARIABLE SO4_icp_Ions_Water2
INSERT VARIABLE SO4_icp_cum AFTER SO4_icp_Ions_Water real
SET FORMULA SO4_icp_cum = SO4_icp_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED SO4_icp_Ions_Water

INSERT VARIABLE Na_Ions_Water2 AFTER SO4_icp_cum real
INSERT VARIABLE Na_Ions_Water AFTER Na_Ions_Water2 real
SET FORMULA Na_Ions_Water2 = Na*"Water_Rate_STB/day"
SET FORMULA Na_Ions_Water = Na_Ions_Water2
ACCUMULATE Na_Ions_Water ascending
REMOVE VARIABLE Na_Ions_Water2
INSERT VARIABLE Na_cum AFTER Na_Ions_Water real
SET FORMULA Na_cum = Na_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Na_Ions_Water

INSERT VARIABLE K_Ions_Water2 AFTER Na_cum real
INSERT VARIABLE K_Ions_Water AFTER K_Ions_Water2 real
SET FORMULA K_Ions_Water2 = K*"Water_Rate_STB/day"
```

```

SET FORMULA K_Ions_Water = K_Ions_Water2
ACCUMULATE K_Ions_Water ascending
REMOVE VARIABLE K_Ions_Water2
INSERT VARIABLE K_cum AFTER K_Ions_Water real
SET FORMULA K_cum = K_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED K_Ions_Water

INSERT VARIABLE Mg_Ions_Water2 AFTER K_cum real
INSERT VARIABLE Mg_Ions_Water AFTER Mg_Ions_Water2 real
SET FORMULA Mg_Ions_Water2 = Mg*"Water_Rate_STB/day"
SET FORMULA Mg_Ions_Water = Mg_Ions_Water2
ACCUMULATE Mg_Ions_Water ascending
REMOVE VARIABLE Mg_Ions_Water2
INSERT VARIABLE Mg_cum AFTER Mg_Ions_Water real
SET FORMULA Mg_cum = Mg_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Mg_Ions_Water

INSERT VARIABLE Fe_Ions_Water2 AFTER Mg_cum real
INSERT VARIABLE Fe_Ions_Water AFTER Fe_Ions_Water2 real
SET FORMULA Fe_Ions_Water2 = Fe*"Water_Rate_STB/day"
SET FORMULA Fe_Ions_Water = Fe_Ions_Water2
ACCUMULATE Fe_Ions_Water ascending
REMOVE VARIABLE Fe_Ions_Water2
INSERT VARIABLE Fe_cum AFTER Fe_Ions_Water real
SET FORMULA Fe_cum = Fe_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Fe_Ions_Water

INSERT VARIABLE Cl_Ions_Water2 AFTER Fe_cum real
INSERT VARIABLE Cl_Ions_Water AFTER Cl_Ions_Water2 real
SET FORMULA Cl_Ions_Water2 = Cl*"Water_Rate_STB/day"
SET FORMULA Cl_Ions_Water = Cl_Ions_Water2
ACCUMULATE Cl_Ions_Water ascending
REMOVE VARIABLE Cl_Ions_Water2
INSERT VARIABLE Cl_cum AFTER Cl_Ions_Water real
SET FORMULA Cl_cum = Cl_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Cl_Ions_Water

INSERT VARIABLE Br_Ions_Water2 AFTER Cl_cum real
INSERT VARIABLE Br_Ions_Water AFTER Br_Ions_Water2 real
SET FORMULA Br_Ions_Water2 = Br*"Water_Rate_STB/day"
SET FORMULA Br_Ions_Water = Br_Ions_Water2
ACCUMULATE Br_Ions_Water ascending
REMOVE VARIABLE Br_Ions_Water2
INSERT VARIABLE Br_cum AFTER Br_Ions_Water real
SET FORMULA Br_cum = Br_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED Br_Ions_Water

INSERT VARIABLE HCO3_Ions_Water2 AFTER Br_cum real
INSERT VARIABLE HCO3_Ions_Water AFTER HCO3_Ions_Water2 real
SET FORMULA HCO3_Ions_Water2 = HCO3*"Water_Rate_STB/day"
SET FORMULA HCO3_Ions_Water = HCO3_Ions_Water2
ACCUMULATE HCO3_Ions_Water ascending
REMOVE VARIABLE HCO3_Ions_Water2
INSERT VARIABLE HCO3_cum AFTER HCO3_Ions_Water real
SET FORMULA HCO3_cum = HCO3_Ions_Water/WatRate_cum
REMOVE VARIABLE NAMED HCO3_Ions_Water

INSERT VARIABLE Ba_cum_Molarity AFTER Ba_cum real
SET FORMULA Ba_cum_Molarity = Ba_cum/137340
INSERT VARIABLE Ca_cum_Molarity AFTER Ca_cum real
SET FORMULA Ca_cum_Molarity = Ca_cum/40080
INSERT VARIABLE Sr_cum_Molarity AFTER Sr_cum real
SET FORMULA Sr_cum_Molarity = Sr_cum/87620
INSERT VARIABLE Na_cum_Molarity AFTER Na_cum real
SET FORMULA Na_cum_Molarity = Na_cum/22990
INSERT VARIABLE Cl_cum_Molarity AFTER Cl_cum real
SET FORMULA Cl_cum_Molarity = Cl_cum/35450
INSERT VARIABLE Br_cum_Molarity AFTER Br_cum real
SET FORMULA Br_cum_Molarity = Br_cum/79900
INSERT VARIABLE SO4_icp_cum_Molarity AFTER SO4_icp_cum real
SET FORMULA SO4_icp_cum_Molarity = SO4_icp_cum/96060
INSERT VARIABLE K_cum_Molarity AFTER K_cum real

```

```

SET FORMULA K_cum Molarity = K_cum/39100
INSERT VARIABLE Mg_cum Molarity AFTER Mg_cum real
SET FORMULA Mg_cum Molarity = Mg_cum/24310
INSERT VARIABLE Fe_cum Molarity AFTER Fe_cum real
SET FORMULA Fe_cum Molarity = Fe_cum/55850
INSERT VARIABLE HCO3_cum Molarity AFTER HCO3_cum real
SET FORMULA HCO3_cum Molarity = HCO3_cum/61018
INSERT VARIABLE Ionic_strength_cum END real
SET FORMULA
Ionic_strength_cum=0.5*(4*Ca_cum Molarity+4*Sr_cum Molarity+4*Ba_cum Molarity+4*SO4_icp_cum
_Molarity+Na_cum Molarity+K_cum Molarity+4*Mg_cum Molarity+4*Fe_cum Molarity+Cl_cum Molarit
y+Br_cum Molarity+HCO3_cum Molarity)
INSERT VARIABLE logKst_cum AFTER Ionic_strength_cum real
SET FORMULA logKst_cum = 1.86+0.0045*Wellhead_Temperature_deg_F_cum-
0.0000012*Wellhead_Temperature_deg_F_cum*Wellhead_Temperature_deg_F_cum+0.000107*Wellhead_P
ressure_psia_cum-2.38*SQRT(Ionic_strength_cum)+0.58*Ionic_strength_cum-
0.0013*SQRT(Ionic_strength_cum)*Wellhead_Temperature_deg_F_cum
INSERT VARIABLE Kst_cum AFTER logKst_cum real
SET FORMULA Kst_cum = 10^logKst_cum
INSERT VARIABLE Ba_cum_precip_mg/l END real
SET FORMULA "Ba_cum_precip_mg/l" = 0
INSERT VARIABLE Ba_cum_precip_M AFTER Ba_cum_precip_mg/l real
SET FORMULA Ba_cum_precip_M = "Ba_cum_precip_mg/l"/137340
INSERT VARIABLE SumM_cum AFTER Kst_cum real
SET FORMULA SumM_cum = Ca_cum Molarity+Sr_cum Molarity+Ba_cum Molarity+Mg_cum Molarity-
Ba_cum_precip_M
INSERT VARIABLE CSO4_cum AFTER SumM_cum real
SET FORMULA CSO4_cum = SO4_icp_cum Molarity - Ba_cum_precip_M
INSERT VARIABLE Free_SO4_M_cum AFTER CSO4_cum real
SET FORMULA Free_SO4_M_cum = (- (1+Kst_cum*(SumM_cum-CSO4_cum)) + SQRT((1+Kst_cum*(SumM_cum-
CSO4_cum))^2+4*Kst_cum*CSO4_cum)) / (2*Kst_cum)
INSERT VARIABLE Free_Ba_M_cum AFTER Free_SO4_M_cum real
SET FORMULA Free_Ba_M_cum = (Ba_cum Molarity-Ba_cum_precip_M) / (1+Kst_cum*Free_SO4_M_cum)
INSERT VARIABLE IS_BaSO4_cum AFTER Free_Ba_M_cum real
SET FORMULA IS_BaSO4_cum = LOG10(Free_Ba_M_cum*Free_SO4_M_cum)+10.03-
0.0048*Wellhead_Temperature_deg_F_cum+0.0000114*Wellhead_Temperature_deg_F_cum*Wellhead_Tem
perature_deg_F_cum-0.000048*Wellhead_Pressure_psia_cum-
2.62*SQRT(Ionic_strength_cum)+0.89*Ionic_strength_cum-
0.002*SQRT(Ionic_strength_cum)*Wellhead_Temperature_deg_F_cum
INSERT VARIABLE FS_BaSO4_cum AFTER IS_BaSO4_cum real
SET FORMULA FS_BaSO4_cum = 10^IS_BaSO4_cum

```