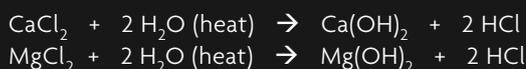


CAUSTIC REPLACEMENT

**Berthold Otzisk, Daniele Ciarletti,
and Juraj Vanovcan, Kurita Europe,**

outline the importance of controlling the concentration of chlorides in the overhead system.

The desalting process of crude oils is an important step in oil refineries, minimising the risk of corrosive damage in downstream operations. Inorganic salts, sand, drilling mud and corrosion byproducts are undesirable materials. The reduction of such impurities to a tolerable minimum is day to day work. Electrical desalters are designed for the removal of inorganic chlorides and significantly reduce corrosion potential. After desalting, the crude oil is fed to the main fractionator at 350 – 380°C, passing heat exchangers and a heater. The remaining magnesium chlorides and calcium chlorides in the crude oil produce hydrogen chloride gas (HCl) by hydrolysis. The hydrogen chloride gas enters the tops section, where it dissolves in condensed water, leading to undesirable results including acid corrosion.



Sodium chloride (NaCl) is far more stable and will not hydrolyse below 500°C. Some refiners take advantage of this effect and inject a diluted sodium hydroxide solution (NaOH) into the desalted crude. The NaOH converts the magnesium chloride and calcium chloride in the

crude oil to sodium chloride without hydrolysis. This will significantly reduce the chloride concentration in the overhead system. Sodium hydroxide is a cheap commodity product, but has a number of drawbacks that either exclude or severely restrict the application, if used for chloride control. Sodium is a catalyst poison and can lead to increased fouling, which is why the treat rate must be monitored very carefully. An oil refinery, where the catalyst for the heavy fuel oil processing was being operated continuously for two years or more, changed the catalyst once a year because of high sodium chloride concentrations.

Difficulties arise when the crude oils contain undesaltable components. The presence of organic chlorides usually causes problems and consequential damage. In general, organic chlorides do not occur naturally in crude oil. Organic chloride contamination often results from the disposal of chlorinated solvents, which are used to clean pipelines or crude oil tankers. They are applied as wax dissolvers in oil

field applications, boost oil extraction by cleaning wells, and accelerate the flow of crude oil. Often, organic chlorides are not monitored as a 'salt increase' in desalted crude oil, but their presence is often paired with significantly higher chloride concentrations in overheads. Subject to chemical structure, some organic chlorides thermally decompose into smaller fragments after desalting, freeing HCl that will enter the overhead section. This leads to increased corrosion and salt fouling. Some organic chlorides like carbon tetrachloride (CCl₄) will not decompose below 380°C. They can cause fouling and corrosion problems in downstream processes, after contact with catalysts.

Controlling chloride concentration

Kurita's patented Ammonium Chloride Free (ACF) technology provides the ability to control the concentration of chlorides in the overhead while using significantly less or no NaOH. This is important

if the necessary dosage of NaOH is not possible or only allowed in limited conditions (Figure 1).

Liquid formulations of the ACF strong organic base are being used for caustic replacement. This base has a high degree of dissociation, immediately reacting with strong acids (e.g. HCl) or its ammonium salts. Magnesium chlorides and calcium chlorides are also converted to ACF chlorides. The reaction product is a quaternary ACF chloride salt, which has a neutral pH of 7, which keeps the metal corrosivity low. These reaction products are more fluid than alkanolamine salts, being used as neutralising amines. Because the base contains no metals, it will not lead to the deterioration of the catalyst in heavy oil desulfurisation units, even if added in excess.

Below 180°C, salts formed by this product would stay in the water phase, due to their hygroscopic nature. At ambient temperature, dried ACF salts become liquid again by absorbing the humidity from the air. In the presence of sour water or by adding wash water, the salts are easily removed with the water phase. Above 180°C the ACF reaction product thermally decomposes into a non-corrosive stable organochloride gas and neutralising amine. The salt concentration of desalted crude oil fluctuates, but it is possible to appropriately control the quantity of chloride ions or pH in the overhead section of the main distillation column. ACF can be injected separately or together with NaOH into the same dosage line. For economic reasons a combination of ACF with much lower caustic addition is a good alternative to reduce the sodium concentration significantly.

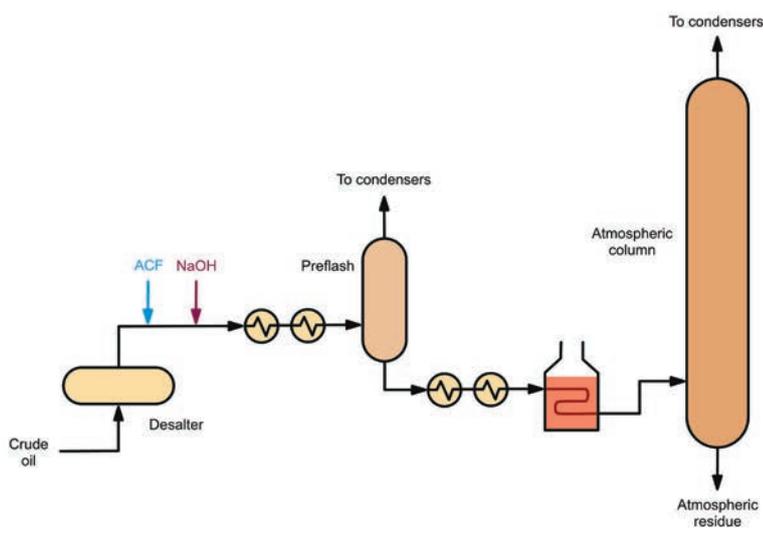


Figure 1. Crude unit with ACF and NaOH injection locations.

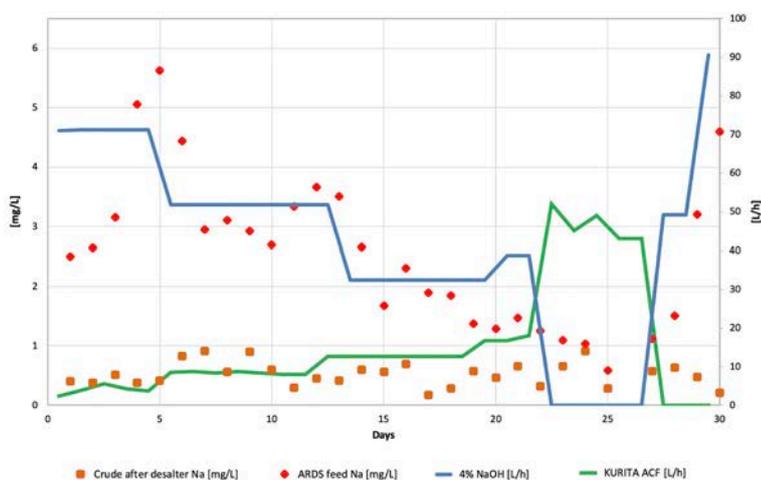


Figure 2. Sodium concentrations in desalted crude oil and ARDS feed.

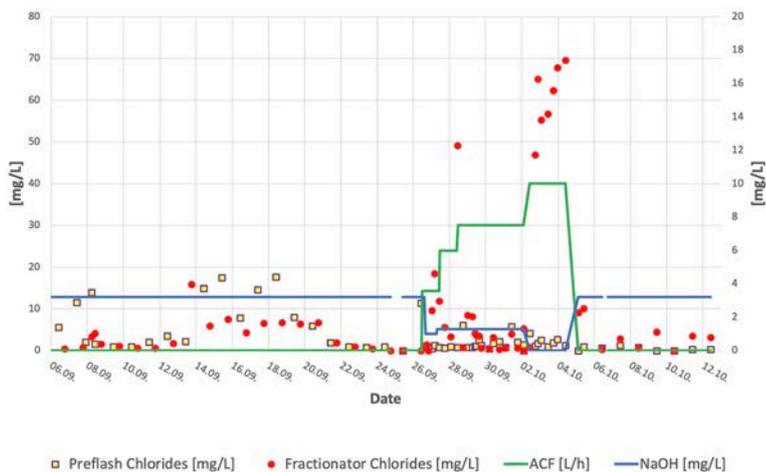


Figure 3. Sodium concentrations in desalted crude oil and ARDS feed.

Case study 1

A crude distillation unit with preflash drum, equipped with a two-stage desalter system was suffering from high chloride levels of about 80 mg/l with sometimes very high peak values up to 180 – 200 mg/l in the overhead system. To reduce the chlorides in the overhead system, high amounts of a 4% NaOH solution had been injected after the second stage of the desalter to form sodium chloride, which remained in the residue finally going to the atmospheric residue desulfurisation (ARDS) unit.

In principle, the salt concentration in the desalted crude oil was always below 1 mg/l. Theoretically that should result in no more than 10 – 20 mg/l chlorides in the sour water of the overhead system. The customer reported roughly 20 l/h of neutralising amine and severe corrosion of the air fin coolers. The high amount of neutralising amine was required to keep the pH in a range of 5.5 to 6.5. It was concluded that additional chloride sources like organic chlorides in the crude oil caused the high chloride concentrations in the sour water phase. The chloride analysis of a desalted crude oil sample confirmed the presence of 5 mg/l organic chlorides. This was believed to be the main reason for the high chloride concentrations in the overhead system.

Because any sodium in the ARDS feed will lead to deactivation of the catalyst, the sodium concentration in the ARDS feed was limited to a maximum 3 mg/l to meet the design data for the ARDS unit. Besides the natural sodium from the crude oil, the main sodium ingress in the ARDS feed was coming from the caustic addition after the desalter. Therefore, the main target for the refinery was to find an alternative additive for the caustic injection to keep the sodium level in the ARDS feed below the design limit. At the same time, it was required that the chloride concentration in the overhead accumulator of the crude unit was kept in the range of 50 – 80 mg/l.

Kurita proposed the replacement of the caustic injection to reduce the sodium concentration in the

ARDS feed. A diluted ACF formulation was injected directly into the NaOH dosage line, which was connected to the crude oil feed line after the second desalter. During a period of one month the injection rate of the diluted formulation was stepwise increased while the caustic injection was decreased until a full replacement of the caustic injection was reached. The sodium concentration in the desalted crude oil and in the feed to the ARDS unit was closely monitored together with the chloride concentration in the overhead accumulator (Figure 2).

From this data the positive effect of the change is clearly visible. During replacement of the caustic injection by ACF, the sodium content in the ARDS feed decreased significantly. Concentration reduction from above 3 mg/l sodium (exceeding the ARDS design limits) to approximately 1 mg/l was achieved when the caustic injection was fully replaced. During the same time the sodium content in the desalted crude was always fluctuating in a range of 0.3 – 0.8 mg/l and the chloride concentration in the overhead accumulator was kept in the desired range of 50 – 80 mg/l. At the end of the monitoring period the ACF injection was stopped and the caustic injection returned to the same dosing rate as usual. Immediately the sodium content in the ARDS feed increased again and after a short period the design level of 3 mg/l was exceeded. This indicated that the reaching of low sodium levels in the ARDS feed was directly related to the application of the ACF technology.

No negative effects on the operation of the whole distillation unit had been observed during the ACF treatment. Moreover, the injection of neutralising amine to the overhead system to control the pH at 5.5 – 6.5 could be reduced by nearly 90%, which gave another commercial benefit to the refinery.

Case study 2

A refinery, where the vacuum residue is fed to an H-Oil unit (Axens proprietary), tested the ACF technology as a replacement for the NaOH. Elevated sodium content in the heavy fuel oil feed negatively interferes with the catalyst regeneration and eventual implementation of HTI's HCAT® hydrocracking process. The H-Oil catalyst is poisoned if sodium exceeds 10 mg/l in the bottom vacuum charge.

During the test phase, NaOH was first partially and then completely replaced by ACF. Sodium in the vacuum residue and pH, chlorides and iron concentrations in the sour water streams of the preflash, main fractionator and vacuum unit overhead accumulator drums were analysed. About 400 water analyses were conducted during the test phase, confirming the significant reduction of chlorides in the preflash sour water and main fractionator accumulator drum. The pH in the main fractionator overhead increased from 6.5 to 7.5. The treat rate of

the neutralising amine was reduced from 1.8 mg/l to 1 mg/l, indicating the reaction of the thermal decomposition product of the ACF chloride formation.

During the 'ACF only injection', the chlorides in the preflash overhead accumulator drum remained low. Chlorides in the main fractionator overhead sour water increased from 50 to 70 mg/l (Figure 3). This observation suggests that a combination of ACF with a low caustic treat rate might be the optimum solution for this crude unit. The combination of a third of the previous dosage of NaOH alongside 6 – 7.5 l/h ACF was found to be the best adjustment. The sodium concentration in the vacuum residue dropped below 10 mg/l. The customer reported a positive impact on downstream units, with better regeneration of spent catalysts, and enabling the introduction of HCAT technology. The consequential increase in conversion rate was the most important benefit for the customer; a 1% increase in conversion equals 40 days production.

Summary

Kurita's technology can provide economic benefits to customers. Case studies highlight a higher ARDS catalyst performance, increased conversion rates to

enable the introduction of HCAT technology, better regeneration of spent catalysts, more stable process conditions, and a reduction of the corrosion potential in the crude distillation overhead system.

Sodium content in the crude oil can be reduced to keep to the design limits of the catalyst, which results in less deactivation and increased service life. Customers benefit from a reduced necessary dosing rate for neutralising amines to control pH in the overhead system.

The ACF technology is an attractive alternative to replace or reduce caustic injections. While NaOH is a commodity product with low purchase costs, a combination of a lower NaOH injection plus ACF treatment provides a good balance between costs, effective chloride control in the sour water overhead, and simultaneous reduction of sodium in crude oil. 

References

1. OTZISK, B., and ACHTEN, J., 'Feeling the chemistry', *Hydrocarbon Engineering*, Vol. 23, No. 12, (December 2018), pp. 50 – 53.
2. GUTZEIT, J., 'Crude Unit Corrosion Guide, A Complete How-To Manual', (2006).
3. KOIZUMI, M., and KARAKI, K., 'Salty business', *Hydrocarbon Engineering*, Vol. 22, No. 11, (November 2017), pp. 72 – 78.