

# PROBLEMS IN CRUDE OIL PRETREATMENT

## REDUCTION OF FRESH WATER CONSUMPTION AND WASTEWATER VOLUME IN ELECTRIC DESALTING UNITS

D. N. Levchenko, N. V. Bergshtein,  
I. B. Kessel', and F. M. Khutoryanskii

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Operating experience with electric desalting units (ÉLOUs) has shown that large amounts of wash water, 10-15% on crude, are needed for thorough desalting. The same amount of wastewater is formed. Because of the high salt content of this wastewater, it cannot be used in the recirculating water system and hence must undergo expensive physical and biological treatment, after which it is discharged into open bodies of water. Because of the increasingly severe requirements for environmental protection, major attention is being given today to the improvement of desalting technology, so as to maximize the removal of chlorides from the crude oil and minimize the consumption of fresh water. This is particularly important for refineries operating with a limited supply of fresh water, such as the Khrasnovodsk, Lisichansk, and Achinsk refineries.

A promising scheme for crude oil desalting with multiple use of the wash water offers the possibility of effective washing of the crude in each stage with a low consumption of fresh water and a small amount of wastewater discharged from the ÉLOU. Several reports have noted the possibility of water reuse in crude oil dehydration and desalting processes [1-3]. Thus far, however, this reuse in most refineries has been confined to the use of drain water from one stage to wash the oil in the preceding stage; recirculation within stages has thus far been accomplished only in the units at the Krasnovodsk refinery [4] and at the Production Association "Kirishinefteorgsintez" [5]. The desirability of such a scheme has not been examined adequately on a theoretical basis. In the present article, we have developed the basis of flow plan for washing crude oil with multiple use of the water.

It is known [6] that in order to ensure effective operation of each stage in an ÉLOU, it is necessary to use 4-7% wash water in the stage. It can be shown by calculation that if the formation water (produced with the oil) is completely mixed with the wash water, much smaller quantities of water will be required. For example, in the two-stage desalting of crude oil containing 0.3% water and 150 mg/liter of salts, complete mixing of the wash water with the formation water, with dewatering of the crude in each stage down to 0.1% to achieve a final salt content of 1 mg/liter, the theoretical water consumption is about 1% of the crude oil volume per stage. In practice, far greater quantities of water are required, since it is difficult to provide complete contact between the drops of formation water and the drops of wash water.

Because of the excess wash water fed to each stage, the salinity of the drain water from these stages is comparatively low, and the difference between the salinity of the water re-

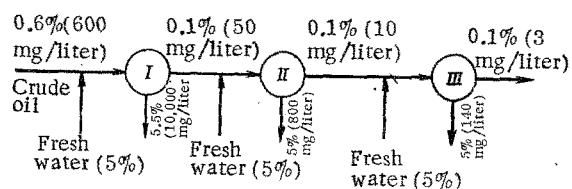


Fig. 1

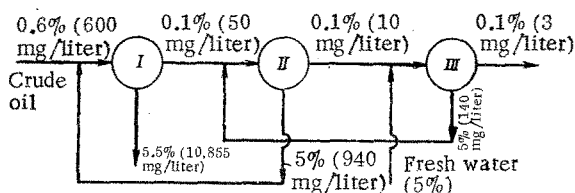


Fig. 2

Fig. 1. Distribution of salts in oil and water through the treating stages with 5% fresh water fed to each stage (total fresh water consumption 15%, total wastewater quantity 15.5%).

Fig. 2. Distribution of salts in oil and water through the desalting states with 5% fresh water fed to the third stage and water returned from state to stage (total fresh water consumption 5%, total quantity of wastewater 5.5%).

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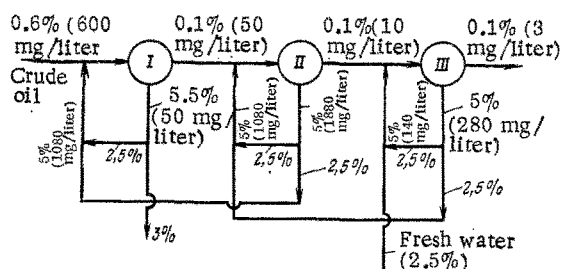


Fig. 3

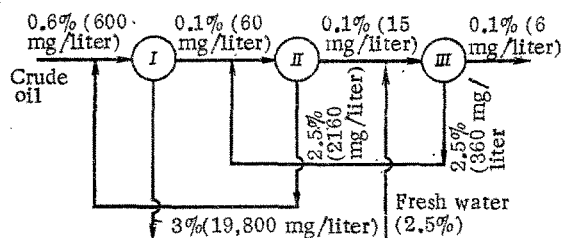


Fig. 4

Fig. 3. Distribution of salts in oil and water through the desalting stages with 2.5% fresh water fed to the third stage, water returned from stage to stage, and 2.5% water recirculated within each stage (total fresh water consumption 2.5%, total volume of wastewater 3%).

Fig. 4. Distribution of salts in oil and water through the desalting stages with 2.5% fresh water fed to the third stage and with wash water returned from stage to stage, without recirculating of water within stages.

maintaining in the crude stage is also quite high. For example, in desalting crude containing 0.1% water and 13 mg/liter of salts, using 4% fresh water to obtain a residual salt content of 3 mg/liter, and that of the drain water is only 250 mg/liter. This means that the required excess of water in each stage can be obtained by recirculating part of the water within this same stage.

There are several versions of the flow plan for washing crude oil with water: with fresh water feed to all stages (Fig. 1), with return of water from stage to stage (Fig. 2), and with return of water plus recirculation of water within each stage (Fig. 3). From a comparison of the salinity (chloride content) of the drain water in the different versions of crude oil washing, it can be seen that the first two versions are approximately equivalent in this respect, but in the third version, the water salinities are almost twice as great. In all cases, this salinity is only about one-tenth that of the water entering with the oil; the water with the oil entering the first stage has a salinity of 100,000 mg/liter, that with the oil entering the third stage 10,000 mg/liter.

This demonstrates that the water consumption can be curtailed not only through reuse from stage to stage, but also by recirculating within each stage. In the first version, the unit as a whole consumes 15% water, in the third version only 2.5%. Thus, multiple reuse of water with return from stage to stage and recirculation within each stage will give substantial reductions in fresh water consumption and in the volume of ELOU waste. Moreover, in cases in which it is impossible to supply the ELOU with the required amount of fresh water, either because of limited availability of fresh water or low capacity of the sewer system and treating facilities, multiple reuse of water will give significant improvements in the quality of the desalted crude.

This is explained as follows. If, for example, a total of 2.5% fresh water is fed to the three stages of the ELOU, less than 1% water is fed to each stage. In this case, the degree of desalting in each stage will be very low, and the residual salt content will be extremely high. Much better results are obtained by feeding 2.5% fresh water to the third stage only, with return of the drain water of the third stage to the second and from the second stage to the first. However, in this case also, because of the deficiency of wash water, the desalting results in all of the stages are poorer than those obtained when 5% water is fed to each stage. The approximate distribution of salts in the oil and water through the stages is shown for this case in Fig. 4.

When we compare the third version that was discussed previously, in which water is both returned from stage to stage and recirculated within stages, with the version using only return of water (Fig. 4), we see that the salt content in the drain water from stage to stage is approximately the same for both of these versions. However, the salt content in the oil from each stage is lower in the version using recirculation. This is achieved by ample washing of the oil with water and a consequent improvement in the contact between drops of the original water and the wash water. High-quality oil desalting can also be achieved with less feed of fresh water from external sources if the condensed water from

the atmospheric/vacuum pipestill unit is used. However, because of the high contents of hydrogen sulfide and ammonia, the condensed water from the distillation unit must first be treated by blowing with steam, as described in [7], for example.

The economics of water reuse are considerably more favorable when considered in the light of the increasingly severe requirements for environmental protection and the consequent use of closed water circulating systems in refineries. When such a cycle is used, the saline wastes are concentrated in a UTOS unit, giving a dry salt residue. The concentration process is extremely expensive, because of the major amounts of heat consumed in driving off the water. The use of wash water recirculation in the desalting process will give a severalfold reduction in the quantity of saline water that must be concentrated and corresponding reductions in the expense of concentrating the ÉLOU waste streams.

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#### INVESTIGATION OF ORGANIC CHLORINE COMPOUNDS IN CRUDE OIL

E. O. Karaulova, D. N. Levchenko,  
N. P. Sosnina, and T. P. Podobaeva

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In the process of crude oil distillation, hydrogen chloride is evolved; this is a highly corrosive material. Until quite recently, it was considered that the hydrogen chloride formed in crude oil distillation comes exclusively from the chlorides of magnesium, calcium, and other metals, these salts being present in the formation water that is emulsified in the oil. Hydrolysis of these chlorides forms hydrogen chloride.

It has been found that even after complete removal of inorganic chlorides in electric desalting units, some crudes will still give hydrogen chloride corrosion in the subsequent distillation. This means that organic chlorine compounds present in the crude must also take part in the formation of hydrogen chloride during distillation. These compounds represent an additional source of the corrosion that destroys crude oil distillation equipment. The organic chlorine compounds are insoluble in water, and hence they are not removed along with the inorganic chlorides during the treatment with wash water in the desalting units; instead, they remain in the oil, decomposing at the distillation temperatures and liberating hydrogen chloride.

Very little information has been reported in the literature, either in the USSR or elsewhere, on the nature, composition, and properties of these organic chlorine compounds. Organic chlorine compounds have been found in a straight-run naphtha cut, and treatment with metallic sodium was proposed to remove these compounds [1]. This same method was used in a study of the distribution of organic halogen compounds in light cuts from petroleum [2]. Results have been reported from determinations of chloride ion in different petroleum cuts [3]. These studies deal only with the organic chlorine compounds present in light cuts of petroleum. Thus far there has been no investigation of such compounds that may be present directly in the crude oil. The methods used in investigating light cuts are not applicable in studying the compounds present in crude oil, since metallic sodium reacts in crude oil not only with

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