Development of nuclear analytical methods against petrochemical corrosion

Thesis of PhD dissertation

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Introduction

Nowadays, the crude oil market changes because of the new trend of the refinery. According to the traders, the European refineries enter into a contract with different region and the crude oil purchases are depend on the actual prices. The crude oil prices is determined by the API (American Petroleum Institute) gravity and the sulphur content of the crude oil, however the different type of crude oils differ from each other in a several ways. The refinery with a capacity of 300 000 barrel/day can gain extra 100 M$ profit, if the refinery margins are increased with 1 $/bbl. On the other hand these benefits are only available without increasing corrosion maintenance costs.

In this study the processing of changing, acidic crude oil with a high salt content was supported with the development of radio analytical technique. During the experiment the low detection limit, the high sensitivity, the detailed analysis of reaction mechanisms, as advantages of activation analysis and radiotracer method were used.

Aims

The aims of the research study are listed below:

1. Analysis of different type of crude oil by the determination of the composition and the development of analytical method to predict the impact of processing.

2. Evaluation of the analytical methods to determine the salt- and the organic chlorine content in crude oil. In these experiments Neutron Activation Analysis was used, as reference method. Standard - and alternative analytical methods were also evaluated in the study.

3. Examination of the corrosion process in high organic acids conditions. The corrosivity and the effects of the corrosion inhibitor were measured in high organic acids model liquid by 14C radiotracer method.

Material and methods

After the analysis of different type of crude oils, the efficiency of the corrosion inhibitors and the analytical methods to determine the amount of corrosive components were evaluated by the application of radio analytical techniques.

The analytical techniques were listed below:

1. Analysis of crude oils:
   - Standard methods: API gravity, acid-, water-, asphaltene- and solid particles content.
   - Specific laboratory model equipment: Emulsification-, and fouling tendency.
   - Incompatibility test
2. Determination of salt- and organic chlorine content:
   - Standard methods
   - X-ray fluorescence spectrometry
   - Neutron Activation Analysis
3. Determination of corrosion inhibitor efficiency:
   - Distillation with soxhlet apparatus
   - Liquid Scintillation Counting

Theses

1. Prediction of the impact of crude oil on the processing

Laboratory techniques were developed to determine the emulsification - and fouling tendencies of crude oils. The application of developed techniques enable the wider characterisation of different type of crude oil than the measurements of the compositions with the determination of the impact on processing.

The conditions of desalter unit operations were simulated to determine the emulsification tendency. For the test of the analytical technique 5 crude oils with 29-49 API gravity and 0,017-2,05 asphaltene content were used. The applicability of the developed analytical methods was justified too by the comparison of the results with the operational parameters of unit.

Fouling tendency of crude oil from different sources was determined without prior information. The correlation between the results and the inorganic contamination, asphaltene contents was detectable.

2. Analytical methods to measure chloride content in crude oils

It was determined that the modified ASTM D7536 method (Standard Test Method for Chlorine in Aromatics by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry) with continous dosage can be applied to measure the chloride and chlorine contents in crude oil. Neutron activation analysis was used in the tests, as reference method.

The relative standard deviation of the results derived from measurements of alternative technique was 10,22 % lower than the relative standard deviation of the test results with standard laboratory technique, when the chloride concentration of crude oil was 8-30 mg/kg.

The results of alternative technique were compared to the results of neutron activation analysis. The deviations of the average results derived from two different techniques were 0,48 mg/kg and 0,28 mg/kg in case of 17,9 mg/kg, 21,9 mg/kg chloride concentration.

The results of neutron activation analysis were compared to the standard technique for determination of chloride and chlorine content of crude oils too. The deviations of the average results derived from these techniques were 0,21 mg/kg and 5,52 mg/kg in case of the same chloride concentration as previous.

3. Investigation of corrosion process induced by organic acid in crude oil

The efficiency of corrosion inhibitor against acetic acid was determined in the laboratory model of distillation column overhead system with radiotracer technique. The radioactivity was measured by liquid scintillation technique. The efficiency of the corrosion inhibitor was 25 % in case of the lowest, 20 ppm dosage concentration, however the concentration dependence of inhibitors could not be detected.

Utilization of the results

The developed laboratory techniques and the results are easily integrable in operating of the modern refinery. The application of its support the processing of low quality, acidic and salty crude oils without increasing corrosion maintenance costs.

Thanks to the developed laboratory model equipment's the emulsification- and fouling tendency of crude oil became easily predictable, while radiotracer method was used to determine the efficiency of corrosion inhibitor against organic acid. These analytical techniques and results help the chemical treatment in the refinery.

The laboratory background of the corrosion protection was developed by the evaluation of the analytical methods to determine the salt- and organic chlorine content in crude oil. The comparison of the results between the activation analysis and non-radio analytical technique overview the application of the well-known standard techniques and the new spectrometric method.

Publications

Publication related to theses

Journal articles

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Conference papers

1. R., Katona; A., Krójer; T., Kovács: Analitikai módszerfejlesztések a hatékony petrolkémiai korrózióvédelmi kontroll biztosítására; 2019. évi VEKOR konferencia, 2019.

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6. R., Katona; R., Locskai; A., Krójer; A., Csordás; T., Kovács: 14C Analysis of organic acids in hydrocarbon mixture, EUROCORR Conference, 2020

Further publications

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5. Katona, R.; A., Rivonkar; Locskai, R.; Bátor, G.; A., Abdelouas; Somlai, J.; Kovács, T.: Tafel-analysis of the AP-CITROX decontamination technology of Inconel alloy 690, Applied Radiation and Isotopes, 110073, 2022

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8. A., Rivonkar; T., Suzuki-Muresan; A., Abdelouas; M., Mokili; Katona, R.; Kovács, T.: Study of existing chemical decontamination methods of radioactive metals with a view on their optimization, International Conference on Radioactive Waste Management: Solutions for Sustainable Future, 199, 2021

9. R., Katona; A., Rivonkar; M., Robin; T., Suzuki-Muresan; A., Abdelouas; G., Bátor; T., Kovács: Optimisation of decontamination of Ni-alloys. VIII. Terrestrial Radioisotopes in Environment. International Conference on Environmental Protection, 14, 2022

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