WHITE PAPER

NORM Decontamination

New exclusive chemical application options for the mitigation of radioactive scale in the oil and gas industry

FQE Chemicals was contacted by a Texas-based petroleum refining company to investigate the use of our product, FQE® NORM-Clear™ PATENTED, developed for the mitigation of radioactive scale contamination. Refinery staff have routinely encountered varying levels of radioactive contamination within their processing equipment. The source of the radioactive scale is the incoming crude oil slate processed by the refinery.

The refinery did not have an analytical assessment of the radioactive scale composition. However, we could presume the presence of some regularly encountered radionuclide species that are transported with well fluids. For example, radium (Ra) prefers the aqueous phase, leading to enhanced concentrations in produced water. Radium is chemically similar to barium (Ba), strontium (Sr), calcium (Ca), and magnesium (Mg), and becomes incorporated in Group II sulfate or carbonate deposits and scales. Conversely, uranium and thorium prefer the solid rock phase and do not dissolve in the aqueous reservoir water nor the resident oil products. As a result, the parent radionuclides remain in the reservoir rock and only appear in natural concentrations at the surface during drilling operations. The daughter nuclides of ^{238} uranium and ^{232} thorium, such as ^{228} radium, ^{226} radium, and ^{210} lead, are prominent species expected to be present. Since both ^{238} uranium and ^{232} thorium have extremely long half-lives, both series are in secular equilibrium on a geological time scale, so that the γ-emission intensities of their respective daughter nuclides can be used for an indication of their parents presence.

While the presence of radioactive elements is evident in processing equipment such as the crude desalters, the refinery had specific concern for the accumulated radioactivity detected within a natural gas plant gas separation towers (depropanizer and debutanizer vessels).

The refinery staff conducted internal radioactivity measurements of the processing equipment using a Ludlum Instruments Geiger Counter and a GM Survey probe. As the measurements for radioactivity were conducted inside the equipment, the relative counts per minute (CPM) were likely inclusive of α, β, and γ-radiation energies. During the previous turnaround, radiation readings taken inside the vessels were in the range of 6,000 CPM. These readings were in excess of their facility safety policies for allowing personnel entry without stringent safety protective measures. The refinery operations management staff began a survey of available technologies that could reduce the presence of radiation and minimize human contact exposures.

Refinery Profile

Natural Gas Plant located in a Texas Refinery

CRUDE CAPACITY

73,000

Barrels per day

TOTAL CAPACITY

90,000

Barrels per day

Health Effects of NORM

The health effects of NORM are a function of the energy transmitted to the body as the radiation dissipates excess energy into living cells, which may result in cellular damage and genetic mutation. In the present framework of radiation protection, effects originated by exposure of humans to radiation are grouped as:

- Deterministic effects: harmful tissue reactions due in large part to the killing/malfunction of cells in large quantities resulting in organ damage following high doses

- Stochastic effects: cancer and heritable effects involving either cancer development in exposed individuals owing to mutation of somatic cells or heritable disease in their offspring owing to mutation of reproductive cells. This is usually associated with long term, low dose, low-level exposure.

Even in the worst case scenarios involving NORM in the oil industry, deterministic effects are never encountered. This is due to the relative low abundances encountered and the tendency for many NORM species to self-absorb, whereby the bulk material matrix absorbs the energy from the underlying decays. In the oil industry, radiation protection in the field of NORM exclusively concerns an adequate control of exposure to low doses where only stochastic effects may occur.

Radiological protection is mainly based on exposure to ionizing radiation; which even at low doses can cause damage to genetic material in cells. This can result in the development of radiation-induced cancer many years later (somatic effects), heritable disease in future generations, and some developmental effects. There are two ways personnel can be exposed to radiation emitted by radioactive material, including NORM: irradiation from external sources, and contamination from inhaled or ingested sources. Irradiation occurs when the material emitting radiation is located outside the human body. Irradiation from external sources occurs in the proximity of the sources and decreases with distance. In the case of NORM, this is usually from contaminated equipment emitting gamma radiation, which is capable of penetrating equipment casing. Personnel frequently working in proximity to contaminated equipment are unaware of the low dose exposure.

It is important to recognize that even with low dose exposure, cellular damage is cumulative and the effects of repeated exposure may not be realized for many years. For this reason, conscientious refiners have understood the importance of radiation accumulation control.

Standard Cleaning Practice

Piping contaminated with NORM

It is standard practice in the oil industry is to abandon contaminated equipment (pumps, piping, etc). Where abandonment is not practical, a typical decontamination process is to use high pressure water blasting at pressures of up to 40,000 psig to physically remove radioactive scales. The waste products (contaminated water and solids) are subsequently collected and disposed of as hazardous material at large expense to the owner. In practice, this process can take several days to complete and can damage machined surfaces.

High pressure water blasting is the practice used by the refiner in this instance. Not only would remediation personnel be exposed to ionizing radiation, but the refiner's operating staff is also routinely exposed to low-level radiation doses from γ-radiation penetrating the vessel case metal. As a safety conscientious employer, the refinery opted to try new technology available in the marketplace to reduce the level of radiation contamination and the potential harm to its employees.

Chemical Approach

FQE Chemicals was contracted to supply FQE® NORM-Clear, which is an exclusive chemistry used to selectively extract radioactive scale deposits. As FQE Chemicals does not perform the service duties for application of its chemical products, it engineers the application process and offers to supply on-site consulting for successful application of its products. The refiner can opt to have any service provider of its choosing perform the application service.

For this project, FQE NORM-Clear was injected into a volume of water added to the vessel. It was decided that a cascade circulation application best suited the timeline for the refinery turnaround. The refiner typically performs a hot-water flush following performance of degassing operations. They had an 18-hour time slot for completion of the hot-water flush in their schedule. Working with the refinery plant supervision, it was decided to add the FQE NORM-Clear to this hot-water flush cycle.

Application conditions for FQE NORM-Clear involves defined operating conditions.

- **Temperature:** circulation water at 160-180° F (71-83° C).
- **pH:** circulation water at a preferred pH range of 11-12.5 using potassium hydroxide as the preferred alkaline source.
- **Fluid Velocity:** circulating water pumped at a flow rate of a minimum of 300 gpm for small volume equipment and a minimum of 1,000 gpm for large volume equipment.
- **Chemical Concentration:** 3-5% v/v of FQE NORM-Clear in suitable make-up water.
- **Make-up Water:** the volumes of make-up water should be limited to a volume required to circulate the water without pump cavitation and to insure the chemical concentration requirement is met.

Case History

FQE® NORM-Clear™
PATENTED

Vessel Type

Depropanizer

Dimensions

(D x L) 13’ 0” 109’ 5-1/2”

Application

Completed by third-party contractor

Project Details

Background Radiation

A survey for background radiation was conducted in the proximity of the process vessels to be cleaned. Background radiation readings were consistently within the range of 1400-1600 CPM using a Ludlum hand-held Geiger counter and a high-sensitivity 2” X 2” NaI scintillation probe.

Chemical Preparation

A typical oil field frac tank was used to hold 20,000 gallons of make-up water. Following completion of the degassing service, a sample of the flush water was taken for evaluation of free oil content. Residual free oil present in a vessel will compromise the performance of the radiation reduction chemical treatment as oil coats the radioactive scales and prevents chemical contact. After the sample of the post-degassing flush water was determined to be acceptable, the water held in the frac tank was pumped into tower using a 4 X 3 centrifugal pump supplied by the service provider.

FQE NORM-Clear was added to the vessel water content using a small injection pump. Injecting FQE NORM-Clear required approximately 8 hours. During the chemical injection time, the vessel was being circulated by use of the 4 X 3 centrifugal pump.

Chemical Circulation

Following completion of the chemical injection, a sample of the circulating water was drawn for pH measurement. The sample result was 10.6 pH, lower than the desired target pH of 12. It was decided not to adjust the pH since the project had experienced significant delays in performance.

The circulating water temperature was much lower than the target temperature at approximately 120° F (49° C). The design was for the plant staff to circulate the treatment water through a reboiler. However, this could not be accomplished, so it was decided to sparge steam into the circulating water to raise the water temperature. The temperature never exceeded 160° F (71° C) during the treatment time.

Radiation Measurements

The essential part of the radiation monitor is the detector, in which the ionization occurs due to the absorption stopping power of α/β-particles or the γ-photons. There is no single instrument capable of detecting all types of radiation (α,β,γ) and energies of the particles (α, β) or photons (γ) emitted by NORM. Under operational conditions, all α- and β-particles will be absorbed by the wall of pipelines and other facility equipment, so that only γ-photons may be detected. However, γ-photons until 200 keV will also be absorbed in a 1.5 cm thick steel wall. Only γ-photons exceeding 200 keV may escape from the operational equipment, so that deposits including the ^{228}Ra and ^{226}Ra subseries may be detected by a meter in an external NORM survey. For these reasons, the measurement for radiation was conducted with a detector containing a NaI scintillation crystal capable of detecting γ-photons through sample containers.

The γ-radiation measurements were as follows:

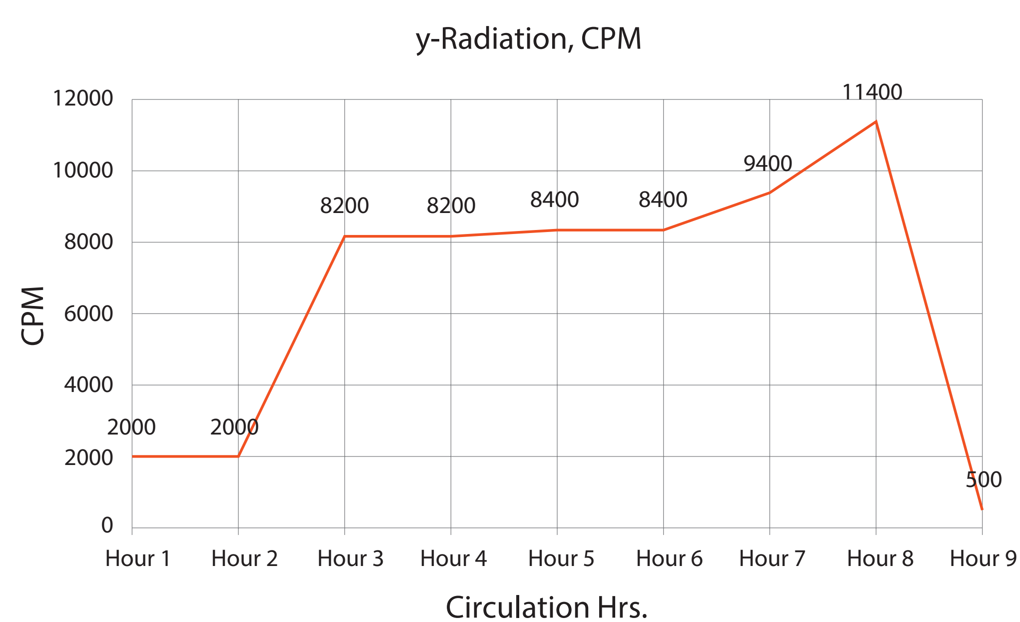
Time	Background, CPM	Sample, CPM	Variance, CPM
11:20	1,500	3,500	2,000
12:20	1,400	3,400	2,000
13:30	1,600	9,800	8,200
14:15	1,600	9,800	8,200
15:15	1,600	10,000	8,400
16:15	1,600	10,000	8,400
19:15	1,600	11,000	9,400
20:15	1,600	13,000	11,400 (end of circulation)
06:00	1,600	2,100	500 (end of water rinse)

The process for measuring chemical function was designed to include testing the circulating water for pH, specific gravity, and γ-radiation. A sample of the circulating water was taken one hour after completion of the FQE NORM-Clear chemical addition. Samples were to be drawn every hour for the test parameters.

During the chemical circulation process, it is expected that the circulation water specific gravity would increase, γ-radiation would increase, and there would be a slight decrease in the pH value.

In practice, the specific gravity values were increasing. However, this parameter was of little value as a live steam sparge into the circulating water prevented meaningful data collection due to the volume dilution occurring.

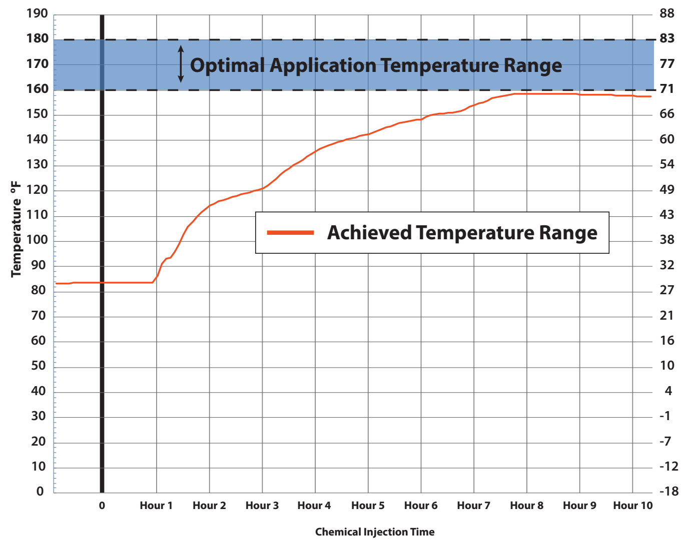
Radiation Counts Per Minute Against Cleaning Time



Challenges Encountered

During the performance of the project, several obstacles/difficulties were encountered that impacted the overall outcome of the work.

Depropanizer Temperature Against Time Chart



Following the vapor-phase degassing stage, the tower was left to cool and the third-party contractor was not advised that the application was to be performed at an elevated temperature. Since arrangements were not made in advance to circulate the water through the tower reboiler, heating had to be conducted through steam sparging. The steam sparge had the effect of diluting the chemical concentration and also making specific gravity data of little value.

The chemical addition to the circulation water was to be done as quickly as possible. It was recommended that a diaphragm or barrel pump be used by the refiner's contractor to expedite the chemical addition. However, a low volume metering pump that was used to inject chemical for the degassing process was repurposed for the FQE NORM-Clear injection, which provided insufficient injection rates. The prolonged chemical addition consumed valuable outage time by applying very low active chemical concentration. The loss of time in circulation at the target full chemical strength reduced the amount of radioactive scale removal.

During the circulation step, the on-site contractor used the 4 X 3 centrifugal pump to circulate the tower liquid volume. The pump in use could only produce approximately 400-500 GPM for liquid circulation. At this flow rate, the tower liquid volume was replaced about once every 45-60 minutes. The liquid circulation flow rate affected the rate of scale removed to expose new scale surface for chemical reaction.

The various time delays encountered during performance of the work limited the ideal treatment conditions.

Table Highlights Where Optimal Chemical Parameters Were Not Met

Parameters Achieved	Optimal Parameters	Differential
Operating Temperature		
90-155° F (32-68°C)	160-180° F (71-82°C)	70-80°F (21-27°C)
pH		
10.4 - 10.8	11.5 - 12	1.1 - 1.2
Chemical Concentration		
1.5 - 2.5%	3 - 5%	50%
Circulation Time		
9 hours	12 - 16 hours	3 - 7 hours

Results

Following the draining of the chemical liquid and a water rinse of the equipment, refinery HSE personnel measured the level of radioactivity interior of the vessel. The detected amount of radioactivity was below the safety policy requirements for personnel entry. Maintenance staff were allowed to enter the tower with standard PPE (gloves, eye protection, and a half-face respirator) and did not require specialized safety equipment nor limited exposure time. Even though optimal chemical conditions were not met, radioactivity readings taken by HSE staff were below 400 CPM on the tower bottom where the majority of the radioactive scale was expected to be found. The chemical treatment water was processed through the site waste-water treatment facility without delay.

Quote from the client:

"I'm confident that if we had a smoother application, meeting all of your specifications we would have been truly 'NORM-Clear'"

In spite of the various delays and complications encountered during the product application, the refinery considered the process to be a huge success and has identified the chemical process as a best practice for the corporation.

Tower Bubble Caps Following Treatment

Tower Tray Following Treatment

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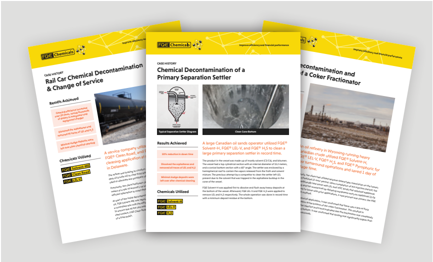

Case Histories

Access a wide range of case histories to learn about the variety of applications our chemicals are utilized for.

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White Papers

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