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Operational and environmental aspects of decontamination of equipment from oil and gas production at ECN, Petten, The Netherlands

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OPERATIONAL AND ENVIRONMENTAL ASPECTS OF DECONTAMINATION OF EQUIPMENT FROM OIL AND GAS PRODUCTION AT ECN, PETTEN, THE NETHERLANDS

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Abstract

The facilities at ECN for treatment of liquid waste prior to its controlled discharge into the North Sea have been in operation since 1963. Although the facilities have been modernized several times the present changes to be implemented are much more drastic. They are directly related to requirements imposed by the authorization under the Law on Pollution of Surface Waters. These requirements involve high demands on the effectiveness of the removal of heavy metals and undissolved solids from the liquid waste streams. The presence of these heavy metals, in particular Pb and Hg, is at least partly related to decontamination of components from oil and gas production. This paper provides a brief overview of the water treatment problems and the solutions envisaged.

Introduction

The facilities for decontamination of the Netherlands Energy Research Foundation (ECN) were originally build and used for removal of radioactive contamination on equipment from the nuclear facilities, e.g. research reactors and laboratories, at the Petten Centre. Liquid wastes arising from decontamination and collected from the various nuclear facilities and laboratories were treated in the water treatment facilities to reduce the activity concentrations in the low-level liquid waste discharged into the North Sea through a 4.5 km long pipeline. From 1963 till 1991 radioactivity and the total volume released yearly were the main characteristics dealt with in the authorization under the Dutch Nuclear Energy law. Since then the situation has changed both with respect to the operational aspects of decontamination and the impact of the limits on waste water characteristics imposed by the implementation of the law on Contamination of Surface Waters (WVO).

Development of deco-activities

In the beginning of the nineties ECN, in close cooperation with Sprengers Oil Field Services, started the development of high-pressure water jetting (HPWJ) for the decontamination of equipment components from oil and gas production, initially tubulars only. Radioactive contamination of these components results from the deposition of either sulfate/carbonate scales containing radium isotopes and/or lead containing Pb-210 on the inner walls of tubulars, valves, X-mass trees, manifolds, etc. It took about 5 years before HPWJ could be applied with confidence to remove scale from tubulars in a semi-automatic radiologically safe system. In mutual consultancy between ECN, the oil industry and the Dutch Government the residual surface contamination limit for free release of decontaminated equipment was set at 0.4 Bq/cm^2 measured as total beta activity.

In the same period the application of HPWJ on non-tabular components with hand-held devices was developed. Although HPWJ is effective on a variety of objects there remained, and still remains, the need for the application of chemical cleaning using alkaline and acid bath's containing detergents on surfaces not accessible by the water-jet. In other cases the shape and size of the objects limits the effectiveness of the water jets impact. This is frequently the case with an increasingly important new category of candidate materials for decontamination: a great variety of objects recovered from loads of scrap of widely different origins by scrap dealers.

Waste water from decontamination

The waste water from decontamination comprises three different flows, one from the application of HWPJ in cleaning of tubulars, one from HPWJ with hand-held devices in the so called "deco-cell" and one from

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chemical cleaning in the "deco-hall". Water from the cleaning of tubulars has always been kept separated from the other two waste water streams because of its high production rate and the need to recover the scale for return to the customer. The other two waste water streams from decontamination were mixed with other waste water from the High Flux Reactor (HFR), Mallinckrodt Medical (MM), from the ECN laundry for protective clothing from radiologically controlled areas and from various radiological laboratories of ECN.

1991 Authorization

Until 1991 concentration limits applied on the waste water discharged into the North Sea concerned only the radioactive components specified in the authorization under the Dutch Nuclear Energy Law. In December 1991 ECN was granted an authorization for discharge of waste water under the Law on Pollution of Surface Waters. This authorization not only specified limits on pollutant concentrations and total volume to be discharged yearly but also prescribed that removal of Cd and Hg from the waste water should be carried out with the best available means and the concentration of the sum of other heavy metals should be limited by the best practicable means. The limits set in the 1991 authorization are presented in Table 1. The authorized limit of the total volume to be discharged was 5000 m^3 per year.

Table 1. Concentration limits from the 1991 authorization for waste water discharged into the North Sea at ECN, Petten.

Component	Concentration limit
Cd	5 μg/l
Hg	5 μg/l
Sum of As, Cr, Cu, Ni, Pb, Sn, Zn	0.5 mg/l
EOCl [1)]	0.1 mg/l
CZV [2)]	1100 mg/l
Undissolved solids	5 mg/l

[1)] Petroleum ether extractable chlorinated organics
[2)] Chemical oxygen demand

In the beginning of the nineties the application of semi-automatic HPWJ on tubulars was still in its development phase and the main waste stream was the mixed one described before. On the basis of promising laboratory tests, treatment with a mixed flocculant Aquastatic-200 was chosen as the best practicable, and possibly the best available, method for this radioactive waste with very changing characteristics.

Water treatment 1992-1995

In the years 1992-1995 the mixed waste stream was treated as shown in figure 1. Aquastatic was added to batches of 25 m^3 waste water in so-called "day-tanks" from which, after settling of the solids, the water was pumped to 100 m3 discharge basins awaiting pumping into the North Sea. The sludge of settled solids was transferred to a sludge tank, then to a sludge hopper for further settling, and finally, dried by slow evaporation in steel drums for transport to the central organization for radioactive waste (COVRA). The effluent flow of HPWJ of tubulars, increased considerably by the end of 1995, was transferred directly to the discharge basins after removal of the quickly settling bulk of solid matter.

The waste water treatment did not fail in bringing the activity concentrations in discharged water well below the limits set in the authorization. However, from the accumulating set of data on effluent monitoring it became clear that the authorized limits on undissolved solids and the sum of heavy metals were frequently exceeded (Figure 2 and 3). By the end of 1995 when proof of an effectively operating water treatment system should have been available to support the application for a new authorization, such proof could clearly not be provided. In the beginning of 1996 ECN, in consultation with the

competent authority, set the goals to have an acceptable application for a new authorization ready by the end of 1996 and a redesigned treatment facility reliably operating approx. 11 months later.

Figure 1. Waste water treatment 1991-1995

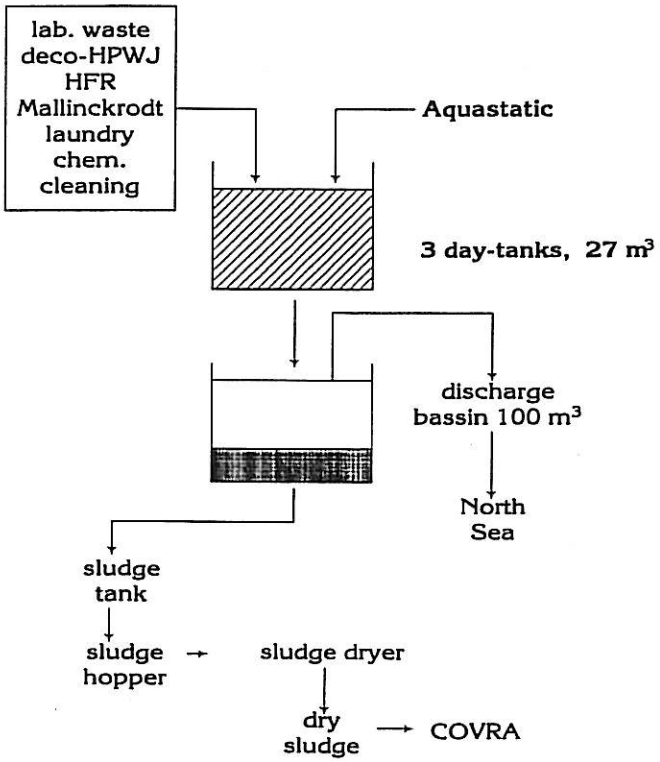


Figure 2. Undissolved solids in samples of discharged water in 1995

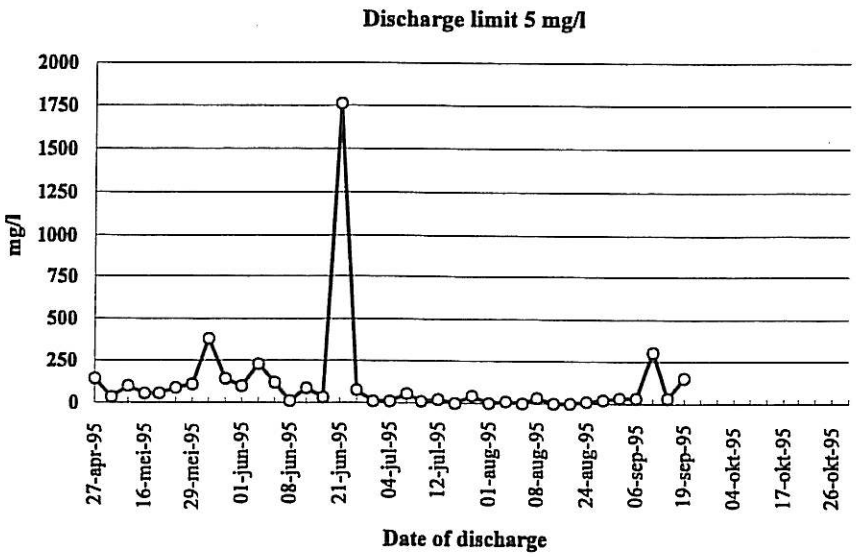
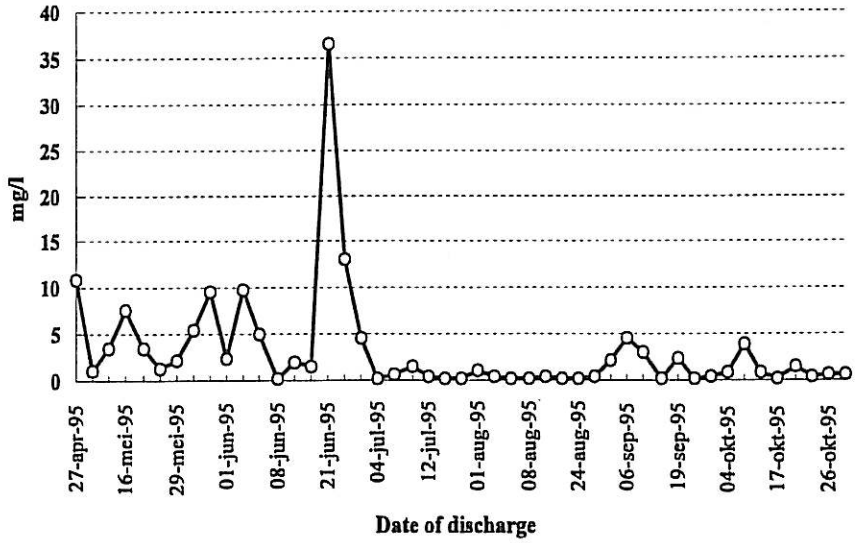


Figure 3. Sum of heavy metals in samples of discharged water in 1995
Discharge limit 0.5 mg/l



The 1996/1997 programme

The programme to reach the goals described above was started in April 1996 and was partly based on the investigations carried out in the preceding years. The programme comprised short-term measures and medium-term research efforts. They are summarized here as follows.

Short-term measures:

1. no waste water any more from former radiological laboratories;
2. replacement of flow-through instrument cooling in radiological laboratories by closed circuit cooling;
3. Interim storage of liquid waste from chemical decontamination because of suspected interference with flocculation;
4. standardisation and registration of each day-tank treatment;
5. use of a 200 m^3 basin for settling of residual suspended solids from effluent of HPWJ of tubulars;
6. bag filtration of effluent from 200 m^3 settling basin before release into discharge basin.

Research programme

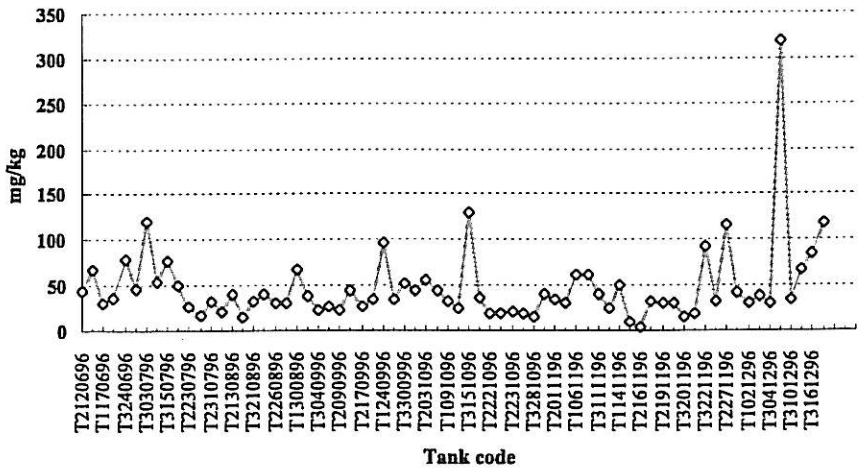
a. long-term monitoring of effluent from day-tanks on undissolved solids, sum of heavy metals and Hg;
b. selection and testing of candidate filtration principles on effluents from day-tanks and HPWJ;
c. selection and testing of alternative day-tank flocculant;
d. testing of candidate filtration principle on effluent from alternative day-tank flocculant;
e. selection and limited testing of treatment system for solids from day-tank flocculation.

Results

The use of a 200 m^3 settling basin for water from HPWJ on tubulars was proven to be effective in reducing the concentration of undissolved solids in the surface layer of the basin to only a few mg/l. Bag filtration reduced the concentration of solids further. However, sometimes the holding capacity of two parallel bag filters was limited to solids from only 25 m^3 or less because of pressure drop over the bag filter holders.

Monitoring of the effluent from day-tanks showed that even after 48 hours settling the concentration of undissolved solids was significantly and rather consistently above the limit of 5 mg/l for water to be discharged (see Figure 4). There were no means available to remove these solids.

Figure 4. Undissolved solids in effluent from day-tank treatments



Analyses of effluent samples, with and without prior filtration at the laboratory over 0.45 µm millipore filters, showed that filtration usually reduced the concentration of the sum of heavy metals to less than 0.5 mg/l (see figure 5). The same effect of millipore filtration was observed for Hg in samples from day-tank effluent as is shown in figure 6. Apparently, residual heavy metals, including Hg, in day-tank effluent and consequently also in the discharged water were largely particle bound. The same observation applied for the heavy metals, mainly Pb and Hg, still remaining in the effluent from HPJW after passage through the settling basin as they could be removed by the bag filter system and, in the laboratory, by millipore filtration.

From the results described above it was concluded that the water treatments applied in 1992-1995 were in principle effective but lacked an effective removal of suspended solids. Therefore, several filtration principles were considered and two systems were tested under the rather uneasy condition of the waste water being radioactive. Dynamic, self cleaning, sand bed filtration appeared not effective enough on the effluent from HPWJ and disappointingly ineffective on batches from day-tank treatments. The results of cross-flow filtration test with ceramic membranes were promising when applied on batches from HPWJ as well as from day-tank treatments. Membranes with a stated pore size of 0.1 µm produced a permeate with very low concentrations of undissolved solids, kept sufficiently long an acceptable permeate flow and their clean water permeate flow could be restored between batch tests by a standard cleaning process specified by the supplier of the test system and the membranes.

Figure 5. Sum of heavy metals in effluent from Aquastatic day-tank treatments

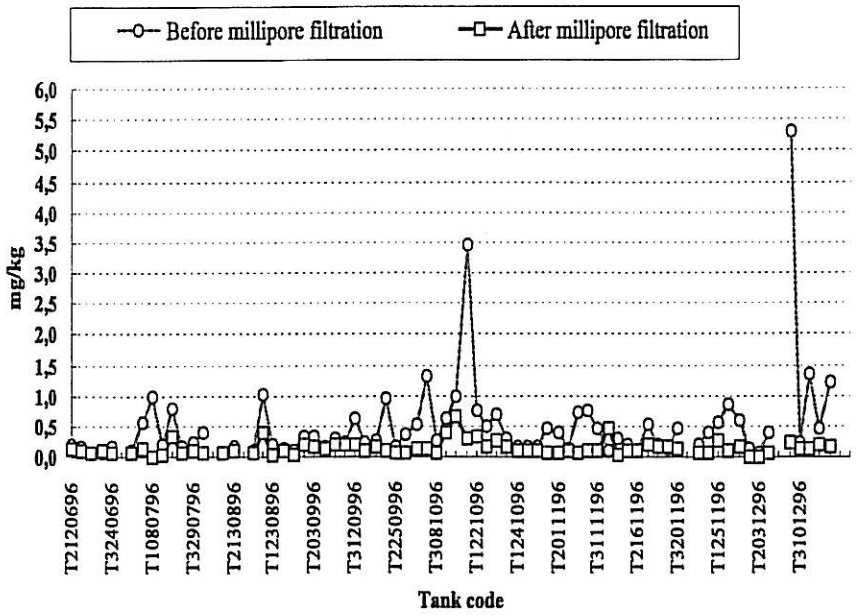
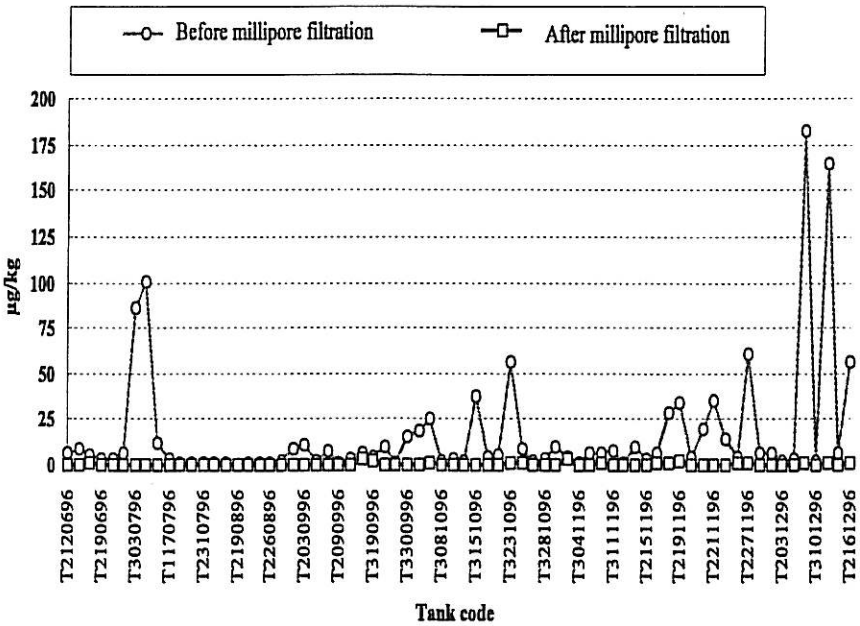


Figure 6. Hg in effluent from Aquastatic day-tank treatments



As an alternative flocculant for Aquastatic in day-tank treatment laboratory tests and full-scale test have been carried out with $Fe(OH)_2$ flocculation. The expected advantages being its lower production rate of solids to be separated, treated and disposed and its lower costs. The full scale tests are not yet finished and evaluated but its effectiveness in removing heavy metals seems not much different from Aquastatic. The same concentration of undissolved solids remains after settling and these solids can effectively be removed by cross-flow filtration with ceramic membranes.

Discussion and conclusions

The environmental aspects of the operation of decontamination facilities at ECN are not solely determined by the decontamination of equipment from oil and gas industries. Firstly, waste water has to be treated because the authorization requires that radioactive contamination must be removed as far as reasonably can be achieved. Secondly, components from other non-nuclear industries are also cleaned to remove radioactive contamination and, inevitably, other contaminants. However, limitations on releases of non-radioactive components laid down in the authorization under the Law on Contamination of Surface Waters causes hard demands on the water treatment performance. These demands certainly comprise a very effective removal of Pb and in particular Hg from the waste water streams. The occurrence of these elements in those streams is largely, but not solely, related to decontamination of components from the oil and gas industry.

On the basis of the research briefly described in this paper ECN is presently laying down the technical specification of its redesigned water treatment facilities. They will comprise separate cross-flow ceramic membrane filtration systems for waste water from day-tank treatments and for the larger stream from HPWJ. In addition a centrifuge unit will be installed for separation of the bulk of the solids from day-tank effluent prior to cross-flow membrane filtration and a dryer unit for conditioning of the solid waste. It is expected that these facilities will be in operation before the end of 1997.