

## **Extending the Range of Organic Compounds that Can Be Destroyed Using the Process of Adsorption Coupled with Electrochemical Regeneration – 13054**

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### **ABSTRACT**

The nuclear industry is not a provider of oils and solvents but uses them in motors, equipment and even in chemical processes to extract valuable products. Currently, for old and contaminated oils and solvents, techniques still exist, such as incineration, but not all the oils and solvents are compatible with this technique because the activities of some components inside the oils are too high to be accepted at the incineration facility. For these oils, an alternative technique needs to be found for treatment. A process developed for water treatment using a technique of adsorption coupled with electrochemical regeneration has been investigated to assess its capability to treat these organic wastes. One of the strengths of the process is its flexibility and adaptation to different compositions of oils. This point is important because, in the AREVA case, there are a lot of small volumes of old oils which need to be re-characterized. It takes time and money to do it especially when oils are contaminated; this is one reason why the technique is interesting to investigate. Tests have been performed with different oils coming from different sites to test the feasibility. Results demonstrate the destruction of a range of organics with regeneration energy requirements of 13.4 - 68.7 kWh/l and offer confidence for the future potential of the process.

### **INTRODUCTION**

Operation and decommissioning of nuclear sites results in the generation of a range of radioactive liquid organic wastes including oils, chelating agents, solvents, corrosion inhibitors, etc. Many of these wastes are difficult to treat using existing technologies (e.g., incineration/cementation/encapsulation). The benefit of oxidation of the organics as a destructive technology has long been recognised and a range of techniques have been investigated. These include chemical [1], photocatalytic [2], electrochemical [3], supercritical water [4], biological [5] and plasma. None of these have yet been proven technically or economically viable.

Arvia has developed a process of adsorption coupled with electrochemical oxidation that has enabled treatment of these organic wastes. This process is based on a novel, highly conducting adsorbent material, Nyex™. Treatment is achieved by dissolving or emulsifying the organic

waste in water, adsorption of the organic component onto the adsorbent and the regeneration of the adsorbent for reuse by electrochemically oxidizing the adsorbed organic.

Examples of difficult-to-treat liquid organic wastes are LLW and ILW oils contaminated with alpha radioactivity at Magnox Ltd nuclear decommissioning site, at Trawsfynydd, in the UK [6]. The current Magnox baseline disposal route for waste oil is incineration, however, this route is not available for significantly contaminated oil and hence these wastes have been identified as orphan wastes or wastes requiring additional treatment (WRAT). Arvia installed a demonstration plant (Figure 1) to destroy 10 litres of these oils. This joint Arvia/Magnox project [7] showed that the oil could be successfully destroyed using an average regeneration energy of 42.5 kWh/l.

The project demonstrated that the majority of the activity remained in the liquid phase (80–90 %), with the remainder on the Nyex<sup>TM</sup> adsorbent. The trial followed the full life-cycle of the plant and components demonstrating that all the waste materials produced could be handled by existing on-site disposal routes. Specifically, the liquid phase and Nyex<sup>TM</sup> were disposed of as follows:

- Liquid was neutralized using 47 % w/v sodium hydroxide to a pH of between 6 and 8 and was successfully discharged to the site active effluent treatment plant (AETP) for disposal via the site active drain.
- The spent Nyex<sup>TM</sup> adsorbent was collected in a 205 litre drum as a wet cake. This equates to less than 50 litres of dry LLW Nyex<sup>TM</sup> to be transported to the UK Low Level Waste Repository for final disposal.



Fig 1. – Arvia Demonstration plant at Trawsfynydd

A key finding of this work was that the various oils could be treated using the same operating parameters demonstrating that the process is robust. Investigating the treatment of a number of different liquid organics will extend the applicability of the process to the nuclear industry.

Recent trials have been performed for AREVA on inactive samples representative of active wastes to be treated like Azolla and Talusia inactive oils, PCBs and a mixture of oil and trichloroethylene (TCE).

## EXPERIMENTAL

Treatability trials were undertaken in one of Arvia's laboratory-scale batch reactors (Figure 2) using non-active solutions. Nyex<sup>TM</sup> (100 g) adsorbent was added to the reactor with 1,000 – 1,500 ml of solution containing a known concentration of the pollutant. Organic solutions were prepared using tap water, either dissolved (for soluble organics) or emulsified (for insoluble organics using an organic emulsifying agent and a high shear mixer) – details in Table 1. The treatment process involved:

1. *Adsorption* – Which is achieved by mixing the Nyex<sup>TM</sup> adsorbent and the effluent through the injection of fluidizing air at the bottom of the reactor, where vigorous mixing and the non-porous nature of the Nyex<sup>TM</sup> adsorbent results in a quick adsorption (typically 15 – 30 minutes).
2. *Sedimentation* – Which results when the fluidising air is switched off and the dense Nyex<sup>TM</sup> particles settle rapidly under the influence of gravity to form a bed (typically 5 – 10 minutes). This bed is formed within a compartment containing a graphite anode and a microporous plastic separator (Daramic<sup>TM</sup>). The graphite cathode is placed behind the separator, with a 0.3 % sodium chloride solution present to provide conductivity between the separator and the electrode.
3. *Electrochemical Destruction* – A direct electric current is passed through the bed which destroys the organic pollutant through anodic oxidation of the organic matter to water, carbon dioxide and small amounts of hydrogen, carbon monoxide and chlorine. This serves to regenerate the adsorbent. The regenerated adsorbent is then ready for immediate re-use and the whole cycle is repeated. Regeneration time varies depending on the organic concentration.

Treatment was achieved over a number adsorption/regeneration cycles. Sodium chloride was used to make up a 0.3 % catholyte brine solution and hydrochloric acid and sodium hydroxide were used for pH adjustment. These were supplied as analytical grade by Fisher. The adsorbent used in the trials was Arvia's Nyex<sup>TM</sup> adsorbent.

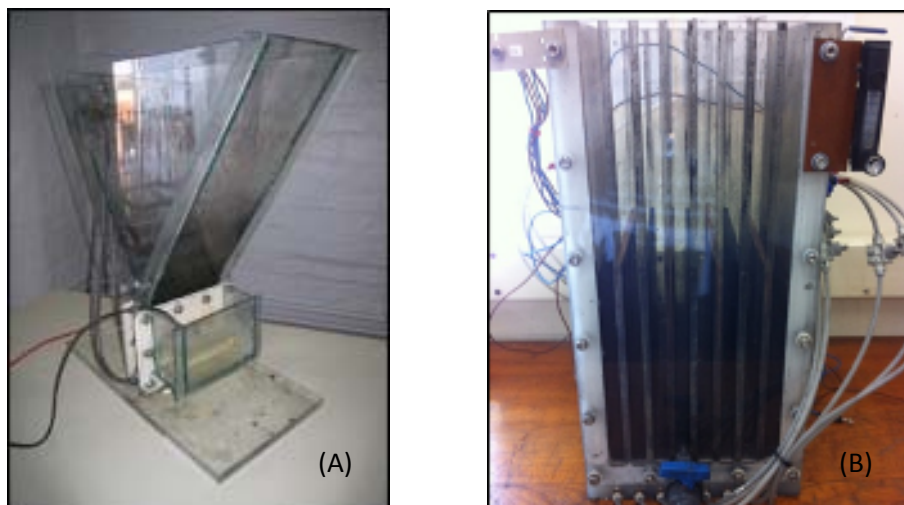


Fig 2. – Laboratory-scale batch reactors - (A) 1-cell system and (B) 4-cell system

### Analysis

The quantity of emulsified oils in the supernatant and on the Nyex<sup>TM</sup> adsorbent was assessed by fluorescence testing (Horiba Jobin Yvon Fluoromax-3 fluorimeter [10]). Dissolved organic concentration was measured in the supernatant by Chemical Oxygen Demand (COD) analysis (using Hach COD 0-1,500 mg/l tubes (with sample diluted to correct range) and a Camlab DR 890 colorimeter). The low-concentration PCB solutions were determined by an external laboratory, Scientific Analysis Laboratories (Manchester, UK).

Table I: Experimental details

Contaminant	Regeneration Time (mins/cycle)	Current (A)	Initial concentration (mg/l)	Treatment method	Analytical method
Hydraulic Oil (Tellus 46)	240	5	670	1	Fluorescence
Diesel (Esso)	240	0.5	670	2	Fluorescence
EDTA*	30	0.5	100	2	COD
Morpholine	30	0.5	200	2	COD
Oily waste sample	240	0.5	0.1 % solution of sample in water	2	COD
Turbine oil (FBK32)	240	0.5	670	2	Fluorescence

AREVA Samples

Contaminant	Regeneration Time (mins/cycle)	Current (A)	Initial concentration (mg/l)	Treatment method	Analytical method
Hydraulic oil (Azolla 32)	60	0.5	670	2	Fluorescence
Marine oil (Talusia HR70)	60	0.5	670	2	Fluorescence
PCB**	10	0.5	0.015	3	External Lab
Azolla/TCE mixture (90/10 %)	TBC	TBC	TBC	TBC	TBC

\* Ethylenediaminetetraacetic acid

\*\* Polychlorinated Biphenyls (PCBs)

Treatments

- 1000 ml of oil emulsion solution was added to the test unit for a number of adsorption/regeneration cycles keeping the same solution within the unit after each cycle. After a number of cycles a further quantity of concentrated oil emulsion was added to give a supernatant oil concentration of 1%. This was repeated after a further number of cycles. Treatment was in Arvia's 4-cell oil test unit.
- 1000 ml of solution was added to the test unit for a number of adsorption/regeneration cycles keeping the same solution within the unit after each cycle.
- 1000 ml of solution was added to the test unit and the supernatant was removed after each adsorption/regeneration cycle and replaced with a further 1000 ml of the same solution.

## RESULTS AND DISCUSSION

### Emulsified Organics

A trial over a number of oil additions was undertaken to assess the performance of the system to remove oil. The hydraulic oil Tellus<sup>TM</sup> 46 was used for this work.

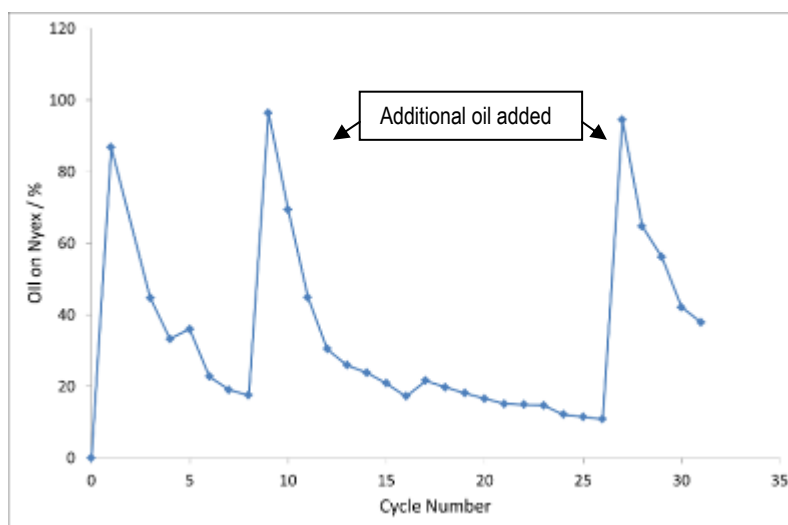


Fig 3. Hydraulic oil on the surface of Nyex<sup>TM</sup> adsorbent over a number of treatment cycles.

This figure highlights a number of important characteristics for the treatment of emulsified oil in water. The first is that adsorption is very rapid and that approximately 90 % of the oil has been adsorbed onto the Nyex<sup>TM</sup> adsorbent surface during the first adsorption cycle after oil addition. Destruction of the oil on the surface takes longer as sufficient charge needs to pass through the system to oxidise the oils. It also demonstrates that the oil destruction rate is proportional to the loading as the rate is greater when there is more oil on the Nyex<sup>TM</sup> adsorbent surface. This suggests that improvement in the operation of a plant can be achieved by modifying the operating parameters such that there is a higher oil concentration on the surface. The similarity in the shape of the graph after each oil addition demonstrates similar performance of the system over a number of cycles. This graph also highlights that the destruction of the final quantity of oil on the surface will take longer as the destruction rate slows. Using different emulsified hydrocarbons (diesel and turbine oil) shows similar results with rapid adsorption after the addition of oil (Figure 4). Regeneration then proceeds at a slower rate as the oil is oxidised. It also suggests the amount of energy required to destroy the oil is dependent on the type of oil, as the regeneration time required to destroy 90% of the oil is achieved in 6 hours with diesel and 24 hours are required to destroy an equivalent amount of turbine oil. Similar results are obtained when a further addition of oil is added after 24 hours. This difference in oil destruction rate may be linked to the viscosity of the oil, but further investigation is required.

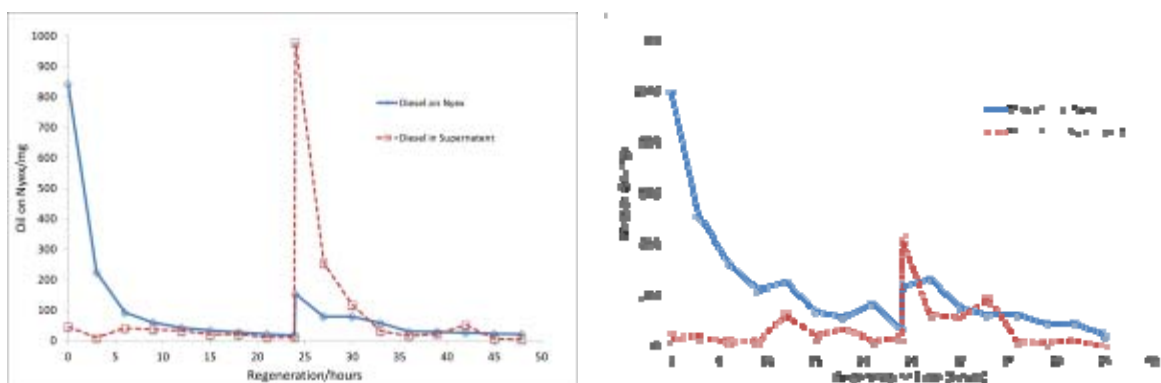


Fig 4. Mass of oil on the Nyex<sup>TM</sup> adsorbent and in the supernatant as measured by fluorescence spectroscopy (Left – Diesel. Right - Turbine oil). Additional oil added after 24 hrs regeneration

Two other oils, a marine oil (Talusia<sup>TM</sup> HR70) and a hydraulic oil (Azolla<sup>TM</sup> 32) have also been investigated (Figure 5). These show similar behaviours to the other emulsified oils tested.

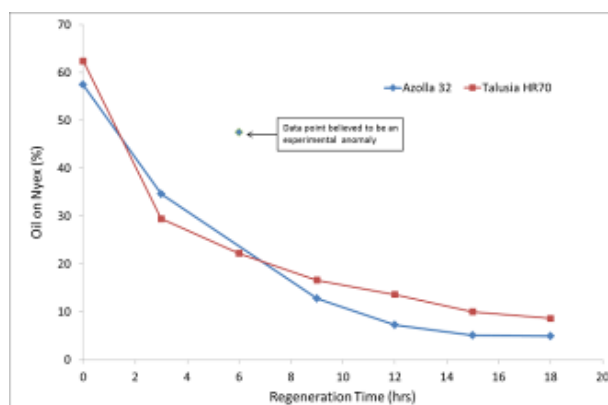


Fig 5. Quantity of oil on the Nyex<sup>TM</sup> adsorbent after a number of adsorption/regeneration cycles

The voltage of the electrochemical cells during regeneration was monitored to allow the energy required for regeneration to be calculated. A trace for the oxidation of the turbine oil is shown in Figure 6. Typically the cells operate at voltages of 4 – 7 Volts.

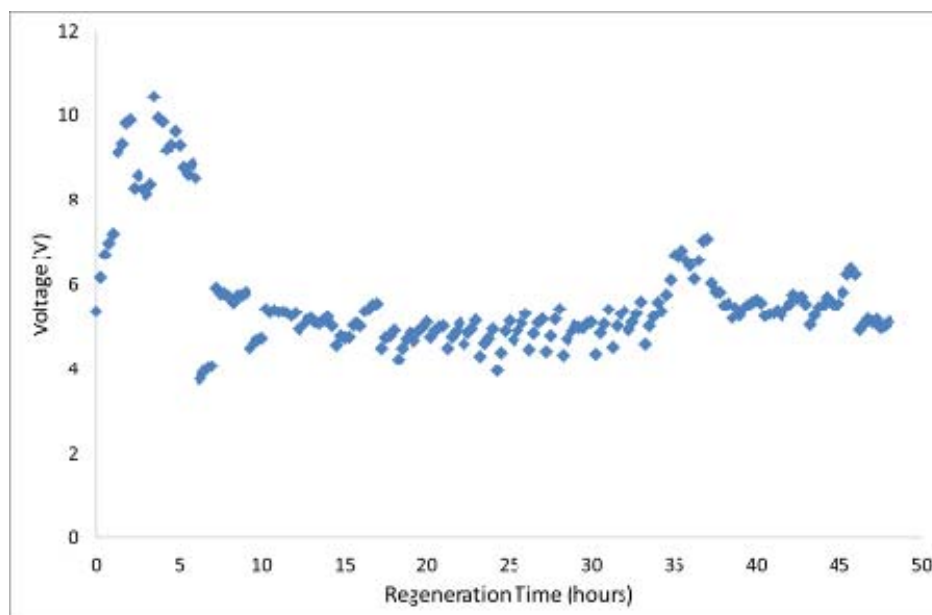


Fig 6. Cell voltages against regeneration time for the destruction of turbine oil

From the data in the above figures, the energy required to destroy a specific quantity of oil can be calculated. As will be appreciated this is dependent on the concentration of oil on the Nyex™ adsorbent surface as the rate of destruction is variable. However for the oils treated, the energy to destroy 90 % of the added oil ranges from 13.4 kWh/l for diesel (destruction of 90 % over 6 hours) to 68.7 kWh/l for Talusia™ (destruction of 90 % over 18 hours).

This regeneration energy range is for plants operating over several orders of magnitude from small laboratory units with electrode areas of 35 cm<sup>2</sup> (13.4 - 68.7 kWh/l) to industrial plant with electrode areas of 45,000 cm<sup>2</sup> (42.5 kWh/l).

### Dissolved Organics

However some of the organics at nuclear sites are soluble in aqueous solution and this section reports on the destruction of these compounds. Ethylenediaminetetraacetic acid (EDTA) and morpholine were also treated and the removal of these (as measured by supernatant COD) is shown in Figure 7. These clearly demonstrate a different behaviour compared with the treatment of emulsified organics. In this case, there is a constant removal of organic (as measured by COD) during each adsorption cycle. This suggests that the mechanism of adsorption is different with the adsorbent having a similar loading independent of the organic concentration. Hence the organics are likely to be adsorbing on active sites on the adsorbent and provided sufficient charge is passed during regeneration to oxidise the organics then the number of sites available for adsorption remains constant and the mass of organic removed per cycle remains the same.



No optimisation work has been undertaken.

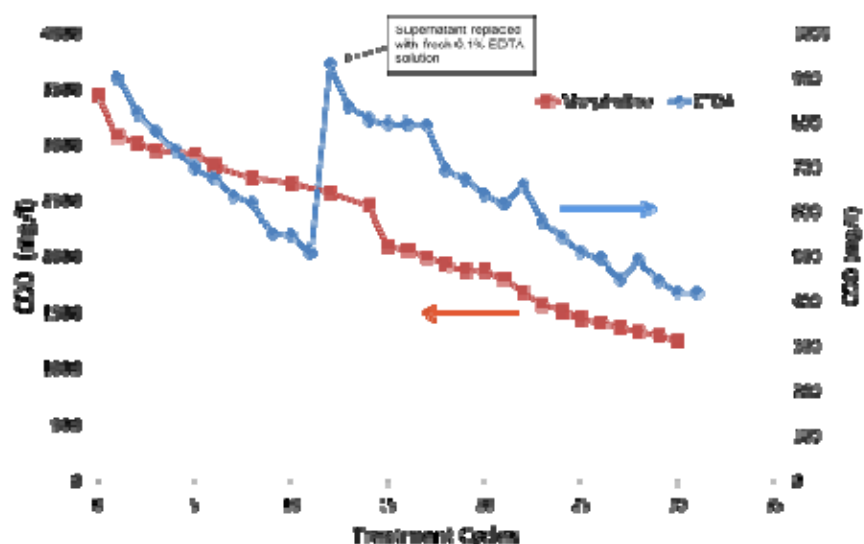


Fig 7. Removal of morpholine (left) and EDTA (right) over a number of treatment cycles by measuring the COD remaining in the supernatant liquid

Calculating the regeneration energy required to destroy 1 litre of morpholine and EDTA gave values of 29.5 and 28.7 kWh/l, respectively. These are within the range of values calculated for the destruction of the emulsified organics, suggesting that although the mechanism of adsorption may be different, the regeneration energy is linked to the charge required to oxidise the organics.

A further group of organic compounds which are sometimes present on nuclear sites are PCBs. A trial was undertaken using a fresh batch of PCB-spiked water for each adsorption/regeneration cycle. Figure 8 shows the percentage removal of the total PCBs after each cycle, demonstrating that if there is no regeneration then the removal efficiency decreases.

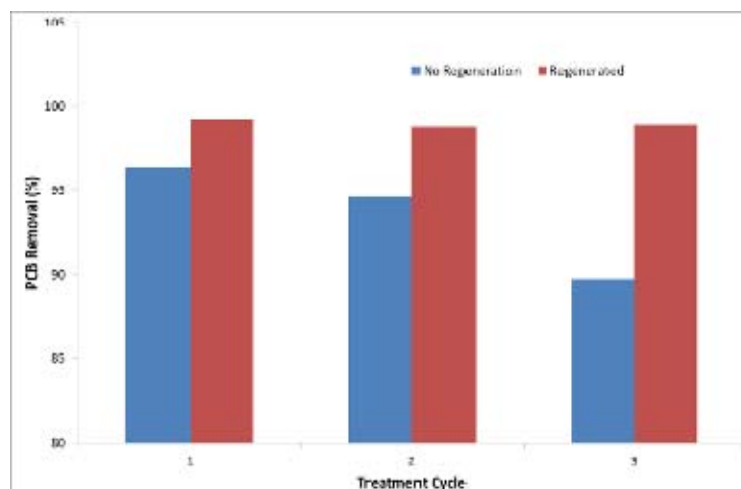


Fig 8. PCB concentration in the supernatant over a number of treatment cycles with and without regeneration when adding fresh PCB solution each cycle

An example of a real (non-active) used oily waste was investigated. The provided sample appeared aqueous containing a small quantity of waste oil. This mixture was a dirty brown colour with a small quantity of waste oil on the surface. This provides an interesting comparison with the separately emulsified and dissolved organic solutions. As can be seen in Figure 9, the first aliquot behaves as an emulsified organic with rapid removal of the organic from the water, but the second aliquot behaves as a dissolved organic.

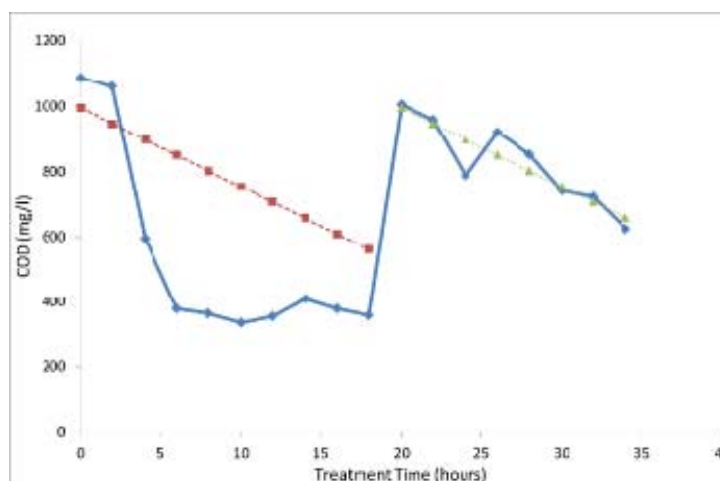


Fig 9. The supernatant COD during the treatment of an aqueous sample containing waste oil added as 2 aliquots. Dotted lines show the predicted CODs based on treatment as a dissolved organic waste

## CONCLUSIONS

This project has shown that the process of adsorption and electrochemical regeneration can be used to treat a number of different organic liquids demonstrating that the process is robust, capable of treating both dissolved and emulsified organics. The energy requirement for organics destruction is between 13.4 - 68.7 kWh/l. This amount of energy is related to the charge required to destroy the organics.

From the AREVA point of view, this technique is promising to take further. The next steps will be to perform tests on radioactive samples and to evaluate the secondary wastes in accordance with the French Waste Agency (ANDRA).

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