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ABSTRACT

Over the past few years SCK•CEN has been focusing on the treatment of tritiated organic liquid waste. The experimental method that we are studying is a complete two-stage combustion with thermal and catalytic oxidation of the organic liquid into tritiated water for further treatment and tritium free off gases for discharge. Our first task involved the treatment of about 200 litres of tritiated organic solvent, with a total activity of around 17TBq. We were able to completely treat this solvent with only limited discharges to the environment. The second application of this technology was a study to treat tritiated organic liquids from the Joint European Torus (JET). We started with cold tests using virgin and inactive oil and liquid scintillation cocktail. As a final step, batches of tritiated feedstock were treated to demonstrate the viability of the process and facility. We conclude that our technology is both technically feasible and safe and can be adapted for the treatment of various categories of problematic tritiated liquid waste, which will undoubtedly be produced in existing installations and in future fusion reactors.

INTRODUCTION

At JET and in future fusion devices various categories of tritiated waste are and will be produced. They will require different detritiation techniques to lower the initial tritium content in the samples and to allow final waste disposal of the partly detritiated material and of all by-products generated in the processes. JET wants to establish a list of verified detritiation techniques which are well assessed, to determine the safest and most cost effective ones. The current internationally adopted strategy is to convert all kinds of tritiated waste into tritiated water, which can then be treated in one water detritiation installation.

Some tritiated waste streams produced today in fusion devices and elsewhere are tritiated pump oil and tritiated liquid scintillation cocktail. In these organic liquids, it seems that the tritium is at least partly bound to non-volatile organic products [1]. Tritiated solvents present another relatively important category of tritiated organic liquid waste.

For the purpose of oxidizing SCK•CEN's own tritiated organic liquid waste, a prototype installation had to be build and operated. The experimental method used is the complete oxidation of the organic liquid into tritiated water and the (almost) complete capture of the product water followed by the discharge of the tritium free off-gases. Later on we had to demonstrate the validity of this method for treating tritiated pump oil and liquid scintillation cocktail from JET.

1. EXPERIMENTAL SET UP

Thermal oxidation followed immediately by catalytic oxidation is, for several reasons, the technology used at SCK•CEN to destroy organic liquids. Destruction efficiencies for different compounds have been shown to exceed 99.99% [2,3]. The process allows direct injection of the liquids or organic vapours. The installation is compact, leak-tight and tritium compatible. Throughputs on the order of a litre per hour are attainable. Reaction-heat can be removed easily with external cooling and/or co-injection of water. Finally the product water can be readily separated from the reactor exhaust.

The heart of the system is a two-stage high temperature Hastelloy reactor illustrated in Fig.1. Organic liquid is atomized and injected into a heated cavity using oxygen as the propellant. Oxidation products and excess oxygen are re-mixed in an alumina diffuser zone downstream of the cavity and passed over heated 0.5% platinum on alumina catalyst. Gases leave the reactor and are separated into condensable and non-condensable fractions. Two sets of heaters are attached to the reactor wall exterior. Typically, the wall temperature of the cavity is set at 750°C while the catalyst temperature is fixed at 700°C. Thermocouples are installed in the reactor to monitor oxidation performance. A nitrogen gas cooling circuit is installed under the cavity heater to remove reaction heat when the need arises.

The tritiated organic liquid waste is injected (possibly preheated) together with co-injection liquid (a mixture of isopropanol and water) and an excess of oxygen. The co-injected liquid is necessary to have a more uniform combustion and/or to increase the sensible heat flow from the reactor when co-injecting water. The working temperature inside the reactor is kept under 1000°C in the thermal zone and below 850°C in the catalytic zone. The nitrogen cooling circuit around the reactor is capable of removing about 2.5 kW. Complete oxidation of the organic fraction is expected in the furnace to produce mainly water and carbon dioxide, provided a stoichiometric equivalent of oxygen is injected. In practice however, at least one stoichiometric equivalent of excess oxygen is required for complete oxidation. The installation can accept liquid flows of up to the order of 1L/h with activities up to 0.2TBq/L.

The gases leaving the reactor are excess oxygen, carbon dioxide and water vapor. Tritium is exclusively present as HTO. Consequently the gases pass through an air-cooler and two condensers. Each condenser is powered by independent refrigerated circulators: the first set at 7°C, the second at 1°C. The bulk of the water vapor is condensed into a tank. Fine water droplets entrained in the carrier stream leaving the tank are removed with a cooled demister and returned to the tank. The remaining gas passes over a molecular sieve bed to scrub out any residual water. Two molecular sieve beds are operated in parallel and permit on-line regeneration without interrupting the processing. A 'polishing' bed downstream of the primary water scrubbers enhances the operating cycle of each molecular sieve bed.

The amount of CO in the gases going to the stack determines the efficiency of the oxidation. The tritium release limit, the feedstock activity and the feedstock throughput set the minimum acceptable tritium trapping efficiency for the water capturing system. The residual tritium activity in the uncondensed gases is measured together with the dew point to determine the efficiency of the trapping of the water.

Depending on the activity of the feedstock different demands are posed on the efficiency of the molecular sieve beds. When treating SCK•CEN's tritiated solvents (specific activities up to 10¹² Bq/L) a dew point of -40°C (neglecting any safety factor) is required to meet emission targets set by SCK•CEN. The active samples coming from JET have very low specific tritium activities (max. 5.10⁶ Bq/L) and in theory only require the use of the condensers.

2. WASTE HANDLING AND PROCESSING

2.1 OXIDATION OF TRITIATED SOLVENTS [4-7]

The Belgian government and the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (ONDRAF/NIRAS) asked SCK•CEN to treat tritiated solvents inherited from the pharmaceutical industry, and to render the liquid into a non-volatile form for long-term storage at Belgoprocess, a nuclear waste processing and interim storage facility in the neighbourhood of SCK•CEN. The waste was documented to be a 95% methanol/water mixture containing 5% impurities comprising petroleum ether, chloroform, and carbon tetrachloride as the major constituents. A total of 178 litres containing a net tritium activity of 16.5TBq, decay corrected to 31/10/2000, was stored in seventy 2.5 litre glass vessels. In turn they were protected in large plastic bottles, nine 200-litre drums and 400-litre drums. In some cases the 400-litre drums had an additional 600 liter overpack. The solvent activity in each vessel ranged from 5 GBq/litre to about 1 TBq/litre. Tritium was the sole radioisotope present.

Several over-arching concerns were addressed to ensure that the solvents could be processed safely. The liquids were volatile, flammable, toxic and radioactive. The integrity of the glass storage vessels could not be assessed until the overpacks were removed. It was assumed that tritium had permeated from the primary containers outwards through the overpack barriers over the years. However the magnitude of tritium accumulation within each air interspace could not be estimated with any confidence until each overpack was unsealed. To minimize the potential for fire and explosion, the inadvertent mixing of oxygen and possibly air with solvent vapors had to be avoided.

Government restrictions on tritium emissions to the atmosphere preclude uncontrolled release of untreated discharges. Consequently streams containing both organic vapors released during all unpacking sequences and water vapor generated during processing needed to be monitored for tritium and if necessary intercepted for treatment. During processing, high conversion efficiencies are required to ensure that the residual Total Organic Carbon (TOC) in the final product meets limitations imposed by ONDRAF/NIRAS.

To address these issues, an infrastructure has been put in place at SCK•CEN to carry out the work with insignificant release to the environment and without compromising worker safety. All work proceeded in one of three large, ventilated walk-in enclosures. The first enclosure houses a glove box for solvent handling and a ventilated metal cabinet for storing pre-processed solvents. A second, located in an adjacent room, houses the oxidation system and its associated water collection system. The third enclosure shares a common wall with the oxidation enclosure and is used for short-term storage of the tritiated product water. The effluent from these enclosures was monitored for tritium and directed to stack. Workers used suits equipped with separate air supplies when working inside the enclosures.

Before processing, samples were taken from each vessel to determine liquid activity and composition to compare results with the available documentation. Surprisingly the waste contained far greater amounts of chlorinated hydrocarbons than expected. Since oxidizing chlorinated hydrocarbons at high temperatures results in the production of wet HCl, several adaptations to the

installation and the working procedure were mandatory. HCl gas formed in the reactor did not pose a significant threat to the reactor because pit corrosion in Hastelloy induced by dry HCl is not significant, even not at high temperature. Wet HCl on the other hand is highly corrosive.

Several changes have been implemented to the oxidation system to ensure the safe treatment of chlorinated feedstock. The most important ones being the co-injection of methanol/water to reduce HCl concentration in the condensate, the neutralization in situ of the condensate, the protection of the molecular sieve beds by a fixed K_2CO_3 bed trap downstream of the condenser and the use of corrosion resistant material (Hastelloy or PTFE).

Following these adjustments, a series of cold commissioning tests were successfully completed in cooperation with Ontario Power Generation Inc. (OPGI) to assure authorities at SCK•CEN that safe handling and destruction of the solvents was possible and that emissions during processing would be negligible.

Subsequently we were able to completely treat the 180 litres of tritiated solvents with only limited discharges to the environment. As shown in Fig.2, less than 0.5% of the activity was vented during normal treatment and liquid discharges were negligibly small. The produced tritiated water has been neutralized and analyzed, and is now waiting for further processing or final disposal.

2.2. OXIDATION OF TRITIATED OILS AND SCINTILLANTS

The next task was a study of the treatment of tritiated organic liquids from the Joint European Torus (JET). JET provided us with cold and hot samples of the pump oil and the liquid scintillation cocktails they use.

2.2.1 Characterization of the Waste

The cold samples were analyzed by VITO (Vlaams Instituut voor Technologisch Onderzoek). The different organic compositions are determined with GC-MS measuring the fractions between C_{10} and C_{40} . Also the flash point (in closed drum), sulfur and chlorine content (by WD-XRF) were measured.

Vacuum pump oil is characterized by its low vapor pressure and inert character at room temperature. The oil should maintain its low vapor pressure and viscosity at working condition in the pump for an extended period of time (tolerance to cracking processes). The basis of vacuum pump oil in most cases is mineral oil with the addition of some additives (less than 5%) containing chloride, sulfur, fluorine or calcium.

P3-pump oil is a mineral oil consisting basically out of carbon and hydrogen. Most molecules have a chain length of more than C_{30} . Some additives like sulfur and nitrogen have been used which may give SO_x and NO_x during oxidation. Pfeiffer TL011 oil on the other hand is basically a carboxylic ester (chain length between C_{21} - C_{30}) with additives. The measurements showed that for the different oils the flashpoint is between 210-242°C and that they have a low sulfur ($\pm 0.1\%$) and chlorine ($< 0.03\%$) content.

Liquid Scintillation Cocktails (LSC) are composed of three products: a primary and secondary scintillator and a solvent. The primary scintillator basically consist out of single aromatic molecules, whereas the secondary contains more complex aromatics (with extra double bounding). The solvent, which is also aromatic, is used to obtain one homogeneous mixture.

The commercial LSCs used at JET are: Oxysolve T Plus, OptiScint Hisafe and OptiScint Hisafe II. The main component of Oxysolve T Plus is trimethyl benzene (60-80%), di-iso-propylnaftaleen (98%) for OptiScint Hisafe and di-iso-propylnaftaleen (70-80%) besides the sulfur containing sodium di-iso-octylsulfosuccinate (10-20%) for OptiScint Hisafe II. The sulfur content can be responsible for SO_x production during oxidation. GC-MS analyses showed a large fraction in the C₁₃-C₂₀ range.

For the liquid scintillation cocktails the flashpoint is between 35-140°C and they have a higher sulfur content than the pump oil (up to 0.75%) but still a low chlorine content (<0.03%). At higher temperatures they can be rather easily oxidized releasing a lot of energy.

2.2.2 Cold runs

The installation was completely inspected and in some places adapted taking into account some modifications necessary to deal with the specific problems of treating oil: new injection nozzles, preheated lines to the nozzle.

Several one-day cold tests were performed to commission the installation, to determine optimal flow rates for the different products and to determine the ideal nozzle configuration. The first test is conducted with the injection nozzle configuration as being used during the oxidation of the methanol/chloroform waste: a single BEX JL 40100 nozzle is used both for injection of the cocktail and injection of the co-injection fluid.

In Fig.3 a temperature profile for different measurement points in the furnace as a function of time is given. At start up the furnace is electrically heated until a temperature of 600 to 700°C. At that point isopropanol (IPA) is injected to further increase the temperature in the furnace until 950°C ('start co-injection'). When a more or less constant temperature profile at the injection point and in the cavity of the furnace is reached the injection of in this case Oxysolve T Plus is started. During the following 20 minutes the flow rates of Oxysolve and the flow rate and composition (IPA/water ratio) of the co-injection fluid is adjusted to obtain a stable temperature at injection of just below 1000°C. To obtain this regime a flow rate of 8 ml/min for Oxysolve and 9 ml/min for water is set. After the Oxysolve-batch was treated the injection was stopped and once again isopropanol is injected through both pump lines to rinse the furnace. At that point there is an initial temperature drop due to the water which is still present in the co-injection line.

It is clear that the reaction principally takes place in the thermal part of the furnace. The temperature in the first area is significantly higher than in the catalytic part, indicating a strongly exothermic reaction. Furthermore it can be seen that there is a uniform distribution of the oxidation in the thermal zone: there is no significant hot spot at the injection point.

This trial exemplifies a successful oxidation: in 85 minutes 634g of Oxysolve T Plus was oxidized together with 0.24L isopropanol and 0.81L water, resulting in 1.9L water with a TOC of 4.5mg/L. With this nozzle configuration and particular liquid scintillation cocktail, the best oxidation ratio was found to be 8ml/min Oxysolve and 9ml/min water.

One of the most critical parts of the furnace is the injection of the waste and the co-injection fluid. The nozzle influences the mixing of the different fluids with the oxygen, the spreading in the furnace and the dimension of the liquid droplets. A good nozzle and nozzle configuration are essential for a good oxidation.

Basically two types of nozzles were used:

- The commercially available BEX JL 40100 which is used for many applications and was used for the treatment of our 178 litres of methanol/chloroform waste. It is a flat spray nozzle with external mixing of fluid and gas.
- The so-called 'Fuchem-nozzle' which is a SCK•CEN design originally developed for other purposes (injection of sodium in a fluidized bed reactor) but adapted for this particular application. The nozzle is a full cone spray nozzle with an adjustable mixing area.

Nozzle efficiency depends on different criteria, the most important ones being: the atomization gas pressure, the liquid and gas flow rate, the viscosity of the liquid. Spray tests were done in open air with both nozzles with isopropanol (IPA), water and pump oil together with oxygen at the working pressure in the furnace. It seemed for both nozzles that a gas flow of 40L/min up to 60L/min O₂ is required to have a good spray of about 10ml/min of liquid. Such a gas flow rate also ensures a more than sufficient oxygen supply for the oxidation in the furnace.

To determine the optimal nozzle three different configurations were tested during separate experiments on cold P3-pump oil:

1. A separate injection of waste and co-injection fluid in the furnace with 2 nozzles of the BEX-type;
2. A mixed injection of waste and co-injection fluid in the furnace with one nozzle:
 - a. One external mixing of fluid and oxygen using the BEX JL40100;
 - b. One adjustable mixing zone area using the Fuchem nozzle.

A summary of the results is given in Table I.

Different selection criteria were used:

- It is important that the major fraction of the oxidation takes place in the free volume before the catalyst;
- A relatively low entrance temperature at the catalyst area is desired in order not to damage the catalyst;
- Low TOC in the product water is important;
- A low co-injection flow limits the production of tritiated water;
- Mechanical condition of the nozzle is inspected after each test. It is important to check for

distortions (maybe caused by excessive high temperatures at the nozzle) and depositions of products (incomplete combustion or salts deposition).

During each experiment about 600g of P3-pump oil was treated in 2h. We observed that the combination with two separate nozzles resulted in poor results. A major part of the combustion occurred at the injection point and consequently significant external cooling of the furnace was needed to keep the temperature at the injection below 1000°C. A high co-injection flow of water was required. No optimal use of the furnace could be made. The results for the mixed injection both with the BEX and the Fuchem nozzle were comparable, except for the fact that the Fuchem nozzle was completely intact after the test while the BEX nozzle showed signs of erosion. Additionally the liquid/oxygen mixing area was easier to adjust with the Fuchem nozzle. This nozzle was used for the active test.

Experiments were also performed with the other available cold samples, resulting in a 2 or 3 times higher volume of product water compared to the volume of the original sample. The TOC of the condensed water was always below 5mg/L. No significant problems occurred.

During the cold runs we were able to commission the installation, choose the best performing nozzle configuration and determine oxidation parameters for all different samples to have an acceptable combustion.

2.2.3 Demonstration on active feedstock

Besides the cold samples of unused pump oil and Liquid Scintillation Cocktails (LSC), JET provided us with active samples. We received two batches of LSC (2 liters Hisafe 5.3MBq/L and 2 litres Oxsolve T 2.73MBq/L) and one batch of pump oil (3 litres P3, 0.3MBq/L).

In 3 different tests, these samples were oxidized using our installation with the Fuchem nozzle. No significant problems arose when treating these products. As an example, the destruction of the active P3 pump oil is further discussed in more detail.

Based on the experience during the cold runs, following flow rates were set after start-up of the installation:

Oxygen flow rate:	50LPM;
Waste injection flow rate:	7ml/min;
Co-injection flow rate:	8ml/min of water/IPA.

The temperature profile during the experiment is given in Fig.4. The oxidation performed as expected. There was enough heat generated in the furnace to maintain an optimal temperature in the furnace. In total 3 litres of waste, 3.3 litres of water, and 0.2 liters of isopropanol were injected. We generated 8.3 liters of condensate with a specific activity of 108.5 kBq/L. The TOC in the water was below our detection limit (2mg/L).

During the test the dew point downstream of the molecular sieves was always below -70°C

corresponding to max. 2.6 ppm H₂O. Taking into account the activity of the produced water (108.5 kBq/L) we can calculate that the maximum specific activity of the exhaust gas is 0.28kBq/m³. Since about 4 m³/h of exhaust gas is produced during the actual combustion and our ventilation flow from the laboratory is 9500 m³/h, the maximum activity at the stack is below 0.12Bq/m³. This is well below our present discharge limit of 7350 Bq/m³ from the tritium laboratories. The tritium discharge to the stack was also measured and found to be less than 0.6% of the treated activity.

CONCLUSIONS

Over the past few years, SCK•CEN has been focusing on the treatment of tritiated organic liquid waste. Our final goal is the reduction of tritiated waste and tritium discharges by treatments that allow convert all tritium to tritiated water.

The experimental method that we are studying is a complete two-stage combustion with thermal and catalytic oxidation of organic liquid into tritiated water for further treatment and tritium free off gases for discharge. Our first task concerned the treatment of about 200 liters of tritiated organic solvent. The main components of the solvent were methanol, chloroform and water. Total activity was around 17TBq. We were able to completely treat this solvent with limited discharges to the environment.

The second application of this technology was a study on the treatment of tritiated organic liquids from the Joint European Torus (JET). It concerned vacuum pump oils and scintillants mixed with water. We refurbished the existing installation and adapted it for the purpose of the treatment of vacuum pump oil. After the commissioning of the upgraded installation, we started cold testing using virgin and inactive oil and liquid scintillation cocktail. As a final step, batches of tritiated feedstock were treated to demonstrate the viability of the process and facility. The treatment produced water with low TOC. A limited tritium discharge to the ventilation was observed.

We conclude that our technology is both technically feasible and safe and can be adapted for the treatment of various categories of problematic tritiated liquid waste, which will undoubtedly be produced in existing installations and in future fusion reactors.

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REFERENCES

- [1]. W.T. Shmayda, Recovery and Enrichment of Tritium from Organic and Aqueous liquids Waste Streams, W53: Experience in the management of wastes from fusion facilities, Culham Science Centre, Abingdon, Oxfordshire, UK, March 2003.

- [2]. L.E. Weaner and D.C. Hoerr, An Evaluation of Laboratory-scale Oxidation of Radioactive Hazardous Organic Materials to Give Legally Disposable Waste, Synthesis and Applications of Isotopically Labeled Compounds 1994, Ed. J. Allen, 1995.
- [3]. L.E. Weaner, D.C. Hoerr and W.T. Shmayda, A Practical Approach to the Destruction of Radioactive Organic Mixtures, Synthesis and Applications of Isotopically Labeled Compounds 1997, Ed. J. R. Heys, 1998.
- [4]. J. Braet, A. Bruggeman, S. Vanderbiesen, W.T. Shmayda, A.B. Antoniazzi, "Treatment of tritiated methanol waste: Experimental set-up and preliminary results," EPRI 2000 Low Level & Mixed Waste Conference, San Antonio, TX, USA, July 19-21, 2000.
- [5]. W.T. Shmayda, A. Bruggeman, J. Braet, S. Vanderbiesen, "Treatment of tritiated solvents, Fusion Science & Technology, Tsukuba, Japan, 12-16 November, 2001, Vol. 41, No.3, p. 721, (2002).
- [6]. A. Bruggeman, J. Braet, S. Vanderbiesen, W.T. Shmayda, Treatment of Tritiated Solvents: Early Experience, 21st Tritium Focus Group Meeting, University of Rochester, Rochester, NY, USA, May 7-9, 2002.
- [7]. J. Braet, A. Bruggeman, Oxidation of tritiated organic waste, W53: Experience in the management of wastes from fusion facilities, Culham Science Centre, Abingdon, Oxfordshire, UK, March 2003.

Nozzle type	Use of thermal part	Cat in > 800°C	TOC (mg/L)	Visual inspection	Co-injection (mL/min)
Separate injection	Bad	No	12,9	Minor damage	12
Mixed injection	Fair	Temporary	2,4	Damage/ Deposition	9
With BEX With Fuchem	Good	No	4,2	No damage	9

Table 1: Selection of nozzle configuration based on selected criteria

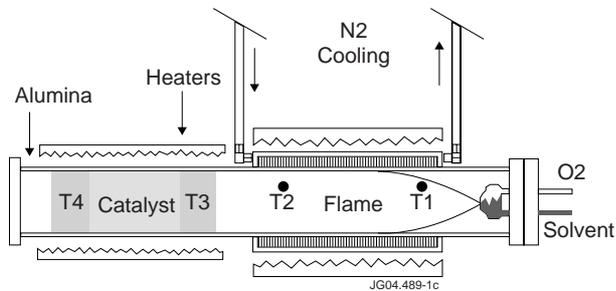


Figure 1: Cross-section of the furnace

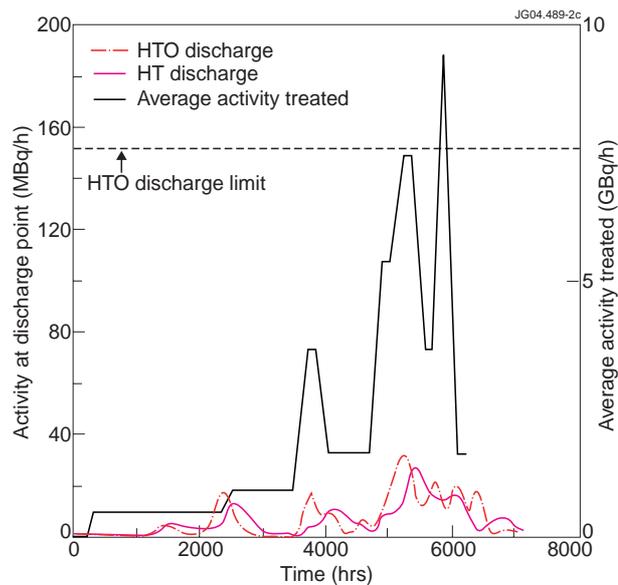


Figure 2: During solvent treatment, the hourly tritium discharge from the tritium laboratory remained far under the limits at that time of 152 MBq/h for HTO and $3.8 \cdot 10^6$ MBq/h for HT. Furthermore less than 0.5% of the solvent's tritium content was discharged to the environment under normal operation.

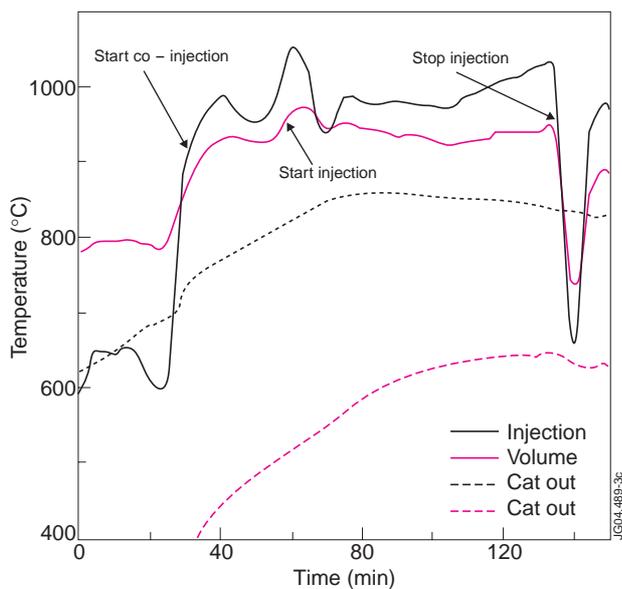


Figure 3: Reaction temperatures oxidizing Oxysolve T Plus

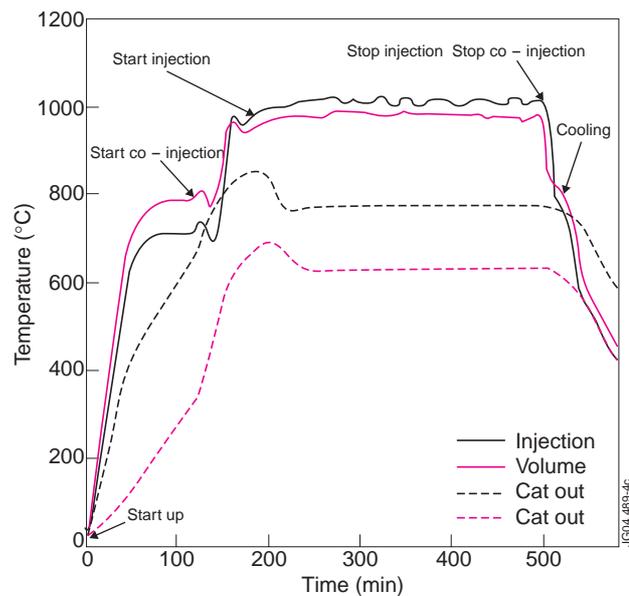


Figure 4: Temperature profiles in the furnace for active P3-pump oil.