

# METHOD OF VOLUME REDUCTION FOR JET SOFT HOUSEKEEPING WASTE

A. N. PEREVEZENTSEV\*† and A. C. BELL *EURATOM/UKAEA Fusion Association  
Culham Science Centre, Abingdon, OX143DB, United Kingdom*

B. M. ANDREEV, I. L. SELIVANENKO, and M. B. ROZENKEVICH  
*Mendeleev University of Chemical Technology, 125047, 9 Miusskaya Square, Moscow, Russia*

Received July 13, 2006

Accepted for Publication December 15, 2006

*The need to protect operators and to control the spread of contamination during Joint European Torus (JET) machine maintenance leads to the generation of soft housekeeping materials contaminated with tritium. These materials consist mostly of various plastics. A portion of the material falls into the category of intermediate-level waste and might need to be processed rather than disposed of as waste. This study deals with combustion in pure oxygen as a primary process for waste volume reduction. A mass reduction factor of 13 or greater has been demonstrated. The facility tested is of scale sufficient to meet the JET needs. The results of inactive experimental trials for the individual plastics and their mixtures are presented. The collection of chlorine-containing compounds released into the process gas during decomposition of polyvinylchloride and issues of complying with air pollution prevention regulations in the European Union have been addressed.*

**KEYWORDS:** *fusion waste, volume reduction, tritiated polymers*

## I. INTRODUCTION

The Joint European Torus (JET) is the world largest tokamak and is capable of operating with tritium plasma. An intensive campaign of operation with tritium, the Deuterium-Tritium Experiment 1 (DTE1) (Ref. 1), was carried out in 1997, resulting in the contamination of the vacuum vessel internals with tritium. While metallic and

graphite wastes have been occasionally generated in a relatively small quantity, intervention and maintenance work on the machine and handling of tritium-contaminated components have led to a nearly constant flow of soft housekeeping materials contaminated with tritium, mainly plastics. A portion of those materials falls into the U.K. category of intermediate-level waste (ILW). The average annual rate of ILW production since DTE1 was evaluated to be  $\sim 1.5$  tonnes.

For example, in the Remote Tile Exchange campaign after DTE1, pressurized suits were used for in-vessel work and in the handling of components removed from the vessel. These operations produced soft waste arising in three main streams. The first stream comprised the actual suit, consisting of gloves, coveralls, disposable clothing, overshoes, and masks, which were worn by the suited operators, the dresser, and the controller in support. The second stream is the soft waste generated during decontamination of the pressurized suits for reuse. This stream also consists of similar types of items plus those parts of suits that are renewed (gloves, filters, etc.). The pressurized suit itself will eventually become a waste once it can no longer be serviced and reused.<sup>2</sup> Finally, plastics have been used for manufacturing tents and isolators needed to control contamination spread.

The tritium content in the current stock of soft housekeeping ILW has been assessed using various bags of waste. The results showed that the tritium concentration varied in the range from 0.05 to 7 GBq/kg with up to 90% of tritium being insoluble in water. This can arise from tritium chemically bound to the carbon chain of polymers through isotopic exchange with hydrogen.<sup>3-5</sup> The tritium distribution in the soft housekeeping ILW was found to be very inhomogeneous even for waste in the same bag. This may be due to the specific source of soft housekeeping material contamination with tritium at JET, which is likely to be a highly tritiated fine carbon dust adherent to the plastics. Carbon dust removed from the vacuum vessel after DTE1 showed a large tritium

\*E-mail: Alexander.Perevezentsev@iter.org

†Current address: ITER Organisation, Caradache, 13108 St. Paul-lez-Durance, France

concentration above 1 TBq/g (Ref. 6). This carbon dust also contains  $\sim 2$  wt% of beryllium, which has been used as a getter to remove gaseous impurities from the vacuum vessel. The plastic becomes internally contaminated by migration of tritium from the adherent dust, possibly in a form of "hot spots."

The soft housekeeping ILW arising from JET operation is currently stored awaiting the availability of a repository for ILW in the United Kingdom. Because of the low density of plastics and the tritium outgassing rate, their eventual disposal as ILW, which is costed on a volume basis, is likely to be an expensive option. A preliminary Best Practical Environmental Option study for JET decommissioning has therefore identified processing such ILW for volume reduction or conversion to LLW as a preferable option.

In scoping studies, decontamination methods already adopted in tritium technology,<sup>7</sup> such as thermal desorption and treatment with surfactant, were tested for detritiation of the JET soft housekeeping ILW. Samples of wastes were heated up to a temperature of 770 K under a flow of dry or wet argon. Tritium released in the form of water vapor was collected using water bubblers. Tritium released in molecular hydrogen form was oxidized by reaction with copper oxide prior to collection. Materials started releasing tritium under dry argon at a temperature as low as 570 K. Most of the tritium was released in the form of water. Tritium release under wet argon started at a higher temperature of 620 K and was in the form of water only. The decomposition of materials with a loss of  $>50\%$  of mass was observed. However, only  $<30\%$  of the initial tritium inventory was released from the plastic. This indicates that a large portion of tritium was chemically bound to the carbon chain of polymers. After being exposed to gaseous tritium/hydrogen mixture plastics present in JET, soft housekeeping waste showed<sup>5</sup> different fractions of the total tritium inventory related to the chemically bound tritium. This tritium was found insoluble in water.

Detritiation using surfactants included treatment with aqueous solutions of various acids, such as phosphoric acid, sulphuric acid, hydrofluoric acid, and nitric acid, and with solutions of sodium hydroxide and hydrogen peroxide. Intensive treatment resulted in removing  $\sim 20\%$  of the tritium inventory with no apparent chemical decomposition of materials.

The aforementioned tests demonstrated that detritiation of the JET soft housekeeping waste requires complete chemical decomposition of the materials. The scoping study was extended to identify and assess further methods that could achieve this. It included various types of pyrolysis/incineration processes, flameless thermal oxidation (for example, steam reforming and molten salt oxidation), plasma methods, and chemical and electrochemical dissolution. A review of the effectiveness, operability, and safety of those methods together with their ease of implementation into the JET environment led to

the selection of three methods for further experimental trials with respect to the decomposition of plastics present in the JET soft housekeeping materials. The first results of studying one of those methods, namely, self-ignited combustion in pure oxygen, are given in this paper. The goals at this stage of development were to demonstrate the achievable factor for mass reduction and to identify the points of technology that need to be addressed for processing JET soft housekeeping ILW.

## II. EXPERIMENT

### II.A. Materials Tested

The JET soft housekeeping ILW includes rubber, cellulose, and three groups of plastics. The plastics consist of polyvinylchloride (PVC), polyurethane (PU), and various plastics of the polyethylene type (PE). The PVC group includes 13 different materials, the PU group includes 4 materials, and the PE group includes 9 materials. An assessment of various materials contained in the JET soft ILW led to the conclusion that the average composition of the wastes could be assumed to be of 30 wt% of PVC, 30 wt% of PU, 30 wt% of PE and rubber, and 10 wt% of cellulose. In addition, the waste could contain a trace of metals, such as stainless steel, copper, and aluminum. In the presence of chlorine and carbon in the waste, these metals might promote the formation of toxic organic compounds during combustion, for example, polychlorinated dibenzo-dioxins/furans (PCDD/PCDFs). Wastes in a bag could contain plastics of one type only or a mixture of different plastics. Because the composition of wastes in bags is unpredictable, the tests were carried out for pure plastics and for various mixtures of plastics. The materials were shredded to  $\sim 10 \times 10$  mm to form a feed stock for the combustion tests.

### II.B. Self-Ignition Combustion Tests

The main element of the test facility, the diagram of which is given in Fig. 1, was the combustion chamber (1). The chamber was thermally insulated (2) to reduce heat losses. The test materials (plastics) were introduced first to the feed tank (3) and then forwarded to the combustion chamber by using a screw conveyer (4). The material was then moved using another screw conveyer (5) through the internal space of the combustion chamber to the outlet connected to the tank (6) for the collection of solid residue. The feed tank can be isolated from the combustion chamber by means of two isolation valves (7). This allowed refeeding the tank and maintaining continuous operation. The combustion chamber can be operated either in a batch or in a continuous mode. A throughput up to 0.5 kg/h can be provided for continuous mode of operation.

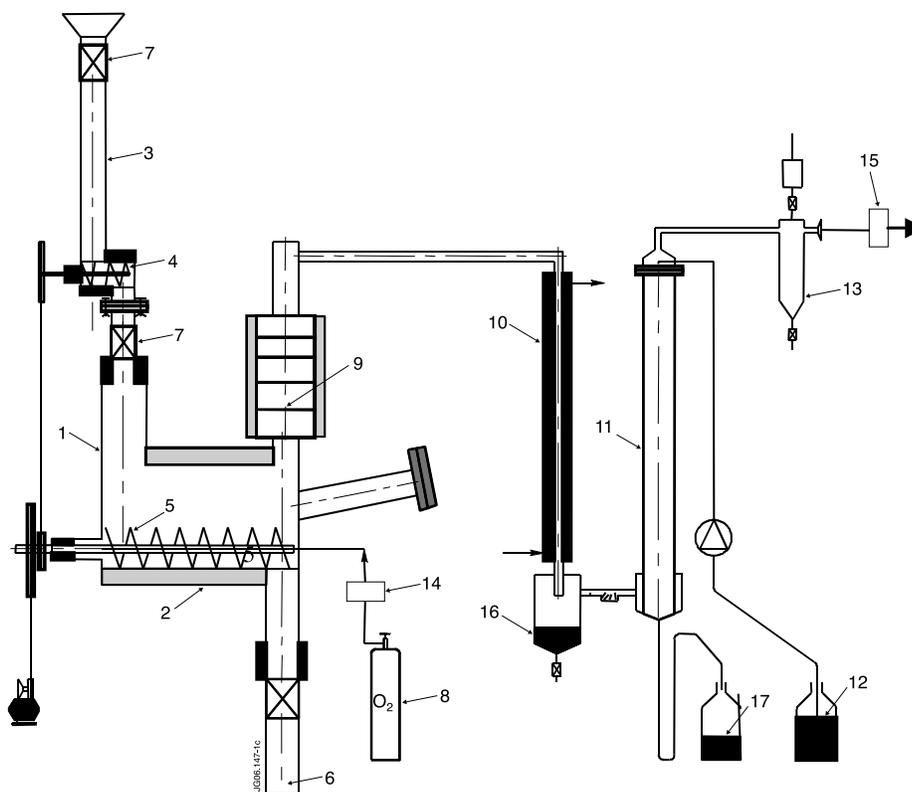


Fig. 1. Schematic of the test facility.

The chamber was initially heated to a temperature sufficient for self-ignition of the plastics. Once combustion started, heat released could be sufficient to maintain self-sustainable combustion. The feed materials entering the heated combustion chamber self-ignite and then continue burning while being moved through the combustion chamber. To provide the oxygen feed (8), the conveyer (5) was equipped with a multipoint injection of oxygen directly to the combustion zone. An excess of oxygen together with the gaseous combustion products leaves the combustion chamber through a porous ceramic filter (9) coated with palladium. The filter traps some solid particles and promotes further oxidation of combustion products. The filter was externally heated to 1120 K at the facility's start-up and then was heated by the process gas formed during the combustion. The process gas consisted of gaseous products and possible liquid and solid particulates entrained by the gas flow.

The process gas was cooled in a tube-in-tube, water-cooled heat exchanger (10), which also removed a fraction of water vapors from the process gas. Condensed water vapors could also absorb part of the chlorine compounds released into the gas phase during combustion. Gases and vapors uncondensed under these conditions as well as particulates were directed to a wet scrubber (11) installed after the heat exchanger. The wet scrubber was a packed bed column charged with an aqueous solution

of sodium carbonate (12). To check the completeness of the acid gas removal from the process gas, the gas already purified in the wet scrubber was passed through a bubbler (13) filled with an aqueous solution of sodium hydroxide. No change in NaOH concentration in the bubbler was observed for all the tests, thus confirming the quantitative removal of water-soluble chlorine compounds by the wet scrubber. As it was also expected that some hydrocarbons, water vapors, and very fine particles could break through the wet scrubber, provision was made for analysis of this stream.

### II.C. Analysis of Combustion Products

Information on the chemical properties of the combustion products is needed to demonstrate that the process would comply with requirements for air pollution prevention and disposal of solid radioactive waste. The combustion of the plastics will produce two direct products: solid residue and process gas. Most of the tritium inventory will be released into the process gas, which needs to be purified of tritium prior to its discharge to the environment. A portion of tritium inventory will remain in the solid residue, requiring it to be disposed of as radioactive waste, which will need to comply with restrictions applied to chemical properties.

The presence of a large quantity of PVC in the JET soft housekeeping waste will lead to generation of sub-products of the combustion process. Pure PVC contains 56.8 wt% of chlorine, which will be mostly released in the form of various chemical compounds into the process gas. Therefore, not only tritium but also chlorine compounds need to be removed from the process gas prior to its discharge to the environment. Because of the presence of chlorine and carbon in the waste and the range of temperatures involved, the formation of very toxic compounds, for example, PCDD/PCDFs, should be expected. Their concentration in the gas discharge from waste-processing facilities is very much restricted in the European Union.<sup>8,9</sup> Other toxic compounds could also be formed, both in the solid residue and in the process gas. Employing a wet scrubber with an aqueous solution as a charge is a widely adopted engineering solution in the chemical industry<sup>10</sup> to purify the process gases from Cl-containing compounds, when chlorine is in the form of anions. The use of a wet scrubber will result in the formation of spent aqueous solution as a subproduct of the waste processing. This solution will contain tritium and compounds of chlorine, mostly chlorides. After chloride removal, tritiated water would be further purified of tritium and discharged to the environment. However, to be discharged the detritiated water needs to comply with requirements applied to the chemical purity of the discharge to the marine or river environment.

As a result of the combustion process and purification of the process gas, three streams need to be tested for the presence of radioactive and chemically hazardous substances: solid residue, purified process gas, and aqueous solutions produced. All three streams were subject to chemical analysis in the test program of this study. Solid residues were collected after each test and divided into two parts for the analysis. One part of solid residue was dissolved in a mixture of nitric, hydrochloric, and hydrofluoric acids and was analyzed for the presence of metals (except cadmium) by using inductively coupled plasma. For cadmium determination, atomic absorption in an air-acetylene flame was used. The second part of the solid residue was used to measure the content of the chloride and hydrogen ions. This was performed by leaching them into bidistilled water for 11 to 25 days followed by chloride titration and pH measurement.

The process gas purified in the wet scrubber was analyzed for the presence of basic gaseous components such as carbon oxides, hydrogen, oxygen, and others plus the content of PCDD/PCDFs. The chemical composition of the process gas was measured using a mass spectrometer with a detection range up to 100 amu and a relative error <15%. Gas purified in the wet scrubber was collected in the buffer tank and then withdrawn for analysis after completion of the test. The content of the PCDD/PCDFs was determined in another test performed at the same set of operation parameters. The process gas after the wet scrubber was passed through a special filter des-

igned for trapping PCDD/PCDFs. The filter was made of ultrathin fiber quartz impregnated with a stationary phase. It also has a layer of polymer sorbent. The filter retained PCDD/PCDFs both adsorbed on solid particles and present in the gas phase. The filter then was used for PCDD/PCDF determination.

Condensate (see 16 in Fig. 1) collected in the heat exchanger and absorbate (see 17 in Fig. 1) collected from the wet scrubber were mixed together and analyzed for the content of inorganic ions; halogen-, nitrogen-, and sulfur-containing organics; the content and the size distribution of solid particles; and the content of the PCDD/PCDFs. The aqueous subproduct was well stirred and then divided into two parts. The first part was filtered to remove the PCDD/PCDFs adsorbed on solid particles. The filter also extracted the PCDD/PCDFs from the liquid. The filter then was used for PCDD/PCDF determination.

The second part of the aqueous subproduct was also filtered to remove solid particles. The filtered liquid was used for analysis of halogen-, nitrogen-, and sulfur-containing organic compounds and inorganic ions. The total mass and the size distribution of solid particles trapped on the filter were measured. An optical microscope was employed to determine the particle size distribution. The size distribution obtained for the particles on the filter does not represent their size distribution in the process gas because it was masked by chemical dissolution and agglomeration occurring in the wet scrubber.

A filtrate from the aqueous subproduct was used to analyze inorganic anions by using an ion chromatograph with a conductometric detector. The detection limits for the halogens,  $\text{NO}_x^-$ , and  $\text{SO}_4^{2-}$  were in the range  $1.1 \times 10^{-11}$  to  $4.8 \times 10^{-11}$  g. A relative standard deviation at a 1-ng level was <4% relative.

The halogen- and sulfur-containing organic compounds were analyzed by extracting them from the aqueous subproduct filtrate into iso-octane, which then was combusted in a flow of pure oxygen at a temperature of 1270 K. Oxygen with oxidation products was bubbled through deionized water, which was then analyzed using an ion chromatograph.

The filters used to remove the PCDD/PCDFs from the process gas and the aqueous subproduct were then subject to PCDD/PCDF extraction from the filter into a mixture of toluene with acetone using an accelerated solvent extraction process. The PCDD/PCDFs were then isolated and preconcentrated using an analytical procedure commonly adopted and certified to measure PCDD/PCDFs. Measuring the content and the composition of the PCDD/PCDFs was carried out using a gas chromatograph connected to a high-resolution mass spectrometer. A known quantity of PCDD/PCDF  $^{13}\text{C}_{12}$ -labeled standard mixture was spiked on the filter prior to use to collect the PCDD/PCDFs from the process gas. This was used as an internal reference mark. A known quantity of

the PCDD/PCDF  $^{13}\text{C}_{12}$ -labeled standard mixture was also added as an internal reference mark to the aqueous subproduct prior to its filtration to determine the PCDD/PCDF content. The standard deviation for PCDD/PCDF determination was no more than 30% relative.

### III. RESULTS AND DISCUSSION

Table I shows the temperatures of self-ignition  $T_{SI}$  and the temperatures sufficient for self-sustainable combustion  $T_{SC}$  measured at atmospheric pressure of pure oxygen using the combustion chamber operated in a batch mode. In these tests a sample of material was loaded into the combustion chamber and then heated at a constant heating rate until it self-ignited at  $T_{SI}$ . After the sample self-ignited, the combustion could stop without complete sample destruction. However, if the temperature of the combustion chamber was high enough to maintain self-sustainable combustion, then a larger extent of decomposition would be achieved. The temperature sufficient for self-sustainable combustion was determined in a series of tests with heating of the plastic samples above the temperature of self-ignition until combustion became self-sustainable. While the temperature of self-ignition was a parameter specific to the plastics, the temperature of self-sustainable combustion depended on the size of the samples and their accessibility to oxygen during combustion. Therefore,  $T_{SC}$  was determined by both the nature of the plastics and the process arrangement in the combustion chamber.

TABLE I  
Temperatures of Self-Ignition and Self-Sustainable Combustion\*

Material	$T_{SI}$ (K)	$T_{SC}$ (K)	Yield of Solid Residue (wt%)
PVC	515 to 730	920 to 1000	1.0 to 30.2 (0.02 to 19.5)
PU	650 to 700	<sup>a</sup>	1.0 to 7.6
PE <sup>b</sup>	585 to 730	930 to 960	1.0 to 35.4 (1.0 to 25.0)
Cellulose	480 to 690	920 to 930	0.1 to 15.4 (0.1 to 11.7)

\*Yield of solid residue is given for combustion at temperature of self-ignition  $T_{SI}$ . Yield of solid residue observed for temperature of self-sustainable combustion  $T_{SC}$  is given in parentheses. Range of parameters observed for different materials in the same group is shown.

<sup>a</sup>No tests at temperatures higher than  $T_{SI}$  were carried out.

<sup>b</sup>This group includes rubber in addition to plastics of PE type.

While the temperatures of self-ignition differ for different materials, a temperature in the range of 900 to 1000 K was sufficient to provide self-sustainable combustion for all of them with a relatively low yield of solid residue. A further increase in the operation temperature will lead to more complete decomposition with a smaller yield of solid residue. For example, a temperature rise to 1100 K led to a reduction of the maximum yield of solid residue for PVC from 19.5 to 11.9 wt%.

Table II presents the results of self-sustainable combustion with a continuous supply of feed materials to the combustion chamber. The continuous mode of the operation permitted the supply of a greater amount of the feed materials to the combustion chamber per test when compared to the batch mode combustion. As a result of the exothermic reactions of plastic oxidation, the continuous mode of operation resulted in the temperature of the combustion chamber being higher than that needed for self-sustainable combustion. The observed yields of the solid residue fall within the range given in Table I. The content of the solid particles collected from the process gas, which is designated here as the yield of solid particulate, was in the range of 5 to 20% of that for the solid residue. The combustion of all tested pure materials and their mixtures achieved a mass reduction factor of 13 or greater.

The basic chemical properties of the solid residue and the solid particulate need to be known to assess the arrangements required for their disposal. Table III shows that there is no correlation between the content of the PVC material in the feed sample and the concentration of chlorine in the solid residue calculated based on the chloride concentrations in water used to leach chloride from a sample of solid residues. The concentrations of chlorine are within about an order of magnitude different for all pure materials and their mixtures. The concentrations of the chlorine in the solid residue produced in the combustion of the PVC materials being similar to that produced in the combustion of non-PVC plastics indicate that the chlorine present in PVC has been mostly released into the gaseous products of combustion.

A large portion of the solid residue did not dissolve in acids, which shows that it consists of carbon and/or nonmetallic inorganic substances. Iron, calcium, nickel, chromium, and aluminum were the major components of the solid residue that were dissolved in acids. Because the solid residue consists mostly of metals and carbon, which absorb tritium in quantities much smaller than plastics,<sup>11</sup> it is likely that the tritium concentration in the solid residue will be smaller than that in the respective original soft housekeeping ILW.

Solid particulates are likely to adsorb PCDD/PCDFs formed in the combustion process. The particulates will be carried out of the combustion chamber with the gas steam and might be a subject to control of both the particulates and the PCDD/PCDFs if this stream is to be discharged to the atmosphere.<sup>8</sup> The gas stream, therefore, would need to be purified of the particulates. The size

TABLE II  
Results of Combustion Tests in Continuous Mode

Test	Feed Composition	$T^a$ (K)	$OR^b$ (m <sup>3</sup> /kg)	Water Yield <sup>c</sup> (kg/kg)	Yield of Solid Residue (wt%)	Yield of Solid Particulate (wt%)	$MRF^d$
A	100% cellulose	890 to 1070	7 (0.7)	0.49 (0.46)	4.3	0.43	21
B	100% PU	1110 to 1220	2.1 (1.4)	0.5 (0.7)	7.3	0.31	13
C	PE plastics and rubber	990 to 1130	3.6 (2.4)	1.05 (1.3)	6.0	1.25	14
D	30% PU, 60% PE, 10% cellulose	990 to 1140	4 (1.9)	0.82 (1.03)	6.5	0.39	14
E	30% PU, 30% PE, 30% PVC, 10% cellulose	1020 to 1110	2.8 (1.5)	0.57 (0.73)	5.0	0.41	18
F	30% PU, 30% PE, 30% PVC, 10% cellulose, metals <sup>e</sup>	920 to 1320	2.7  (1.5)	0.65  (0.73)	5.3	1.16	15
G	100% PVC	1050 to 1570	1.6 (0.9)	0.21 (0.29)	5.9	—	17
H	100% PVC, metals <sup>e</sup>	1070 to 1470	1.8 (0.9)	0.25 (0.29)	6.5	0.44	14

<sup>a</sup>This is the temperature in the combustion chamber during the test.

<sup>b</sup>Oxygen ratio  $OR$  is quantity of oxygen fed to the combustion chamber per mass of feed material. The stoichiometric values are given in parentheses.

<sup>c</sup>Quantity of water collected in the combustion tests per mass of feed (theoretical values are given in parentheses).

<sup>d</sup>Mass reduction factor  $MRF$  was calculated as a ratio of mass of original sample to sum of solid residue and solid particulate masses.

<sup>e</sup>Steel, copper, and aluminum with content of 0.5 wt% each were added to plastics to study effect of metal's presence in the JET soft housekeeping ILW.

TABLE III  
Chemical Composition of Solid Residue

Parameter	Test							
	A	B	C	D	E	F	G	H
Content of chlorine in solid residue (g/kg)	28.4	7.3	20.3	14.9	95.9	26.1	11.6	11.7
Concentration of Cl <sup>-</sup> in leaching water (mol/ℓ)	0.040	0.010	0.029	0.021	0.135	0.037	0.016	0.016
Fraction of solid residue insoluble in acids (wt%)	73	58	49	52	31	60	42	62
Content of elements in solid residue (g/kg)								
Si	0.04	0.1	0.2	0.04	0.01	0.02	0.2	0.08
Al	31.7	13.8	36.9	1.7	18.0	4.1	4.5	2.2
Mg	3.9	0.3	1.0	1.0	2.0	1.0	0.3	0.5
Ca	85.2	14.1	17.2	37.6	91.4	35.8	20.1	18.8
Fe	262.3	304.6	253.0	419.4	169.9	195.4	459.5	252.1
Mn	4.7	4.3	4.0	5.4	2.7	4.1	7.1	5.9
Ti	4.2	1.2	2.9	2.9	2.0	1.0	2.3	1.3
Na	10.3	0.3	0.4	0.3	5.7	0.7	0.4	0.4
Cu	2.9	2.7	2.6	8.0	1.5	8.4	4.2	3.5
Ni	23.1	24.9	24.5	27.8	17.3	22.0	28.3	—
Co	0.2	0.2	0.1	0.1	0.4	0.1	0.1	0.2
Cr	28.2	2.2	16.6	14.4	35.0	10.5	17.5	14.2

TABLE IV  
Size Distribution of Solid Particles Collected in the Condenser and the Wet Scrubber

Test	Fraction of Particles (Percent of Quantity of Particles)						
	<25 $\mu\text{m}$	<50 $\mu\text{m}$	<100 $\mu\text{m}$	<150 $\mu\text{m}$	<300 $\mu\text{m}$	<500 $\mu\text{m}$	>500 $\mu\text{m}$
A	71	20	6	2	1	0	0
B	72	18	6	3	1	0	0
C	8	29	20	26	13	3	1
D	55	26	11	7	1	0	0
E	51	21	13	6	4	3	2
F	61	17	11	3	3	4	1
G	44	22	12	10	7	5	0
H	13	24	35	20	6	2	0

distribution is a parameter important to effectively trap particulates generated in the combustion chamber. A large portion of those particulates was removed from the process gas using the wet scrubber. The size distribution of the particulates collected by the wet scrubber was measured using an optical microscope with a detection limit of 5  $\mu\text{m}$ . The results are presented in Table IV. The largest portion of the particulates was between 5 and 25  $\mu\text{m}$ . It is likely that the solid particulates were agglomerating as a result of the wet scrubber operation and that therefore, the particulates entering the wet scrubber could have been of sizes smaller than those illustrated in Table IV. The effectiveness of particulate removal from the gaseous stream reduces with a decrease in their size. Wet scrubbers of a packed bed type are known to be efficient for removal of particulates of 5  $\mu\text{m}$  or larger.<sup>10</sup> Some of the solid particles broke through the wet scrubber and were collected by the ultrafine filter employed to measure the PCDD/PCDF content in the process gas.

Mass-spectrometric analysis of the process gas purified in the wet scrubber showed oxygen, carbon oxides, and argon as the only detected components. This showed that combustion products, which contain chlorine compounds soluble in the wet scrubber charge, were quantitatively removed from the process gas.

Table V presents the content of halogen-containing compounds removed from the process gas in the liquids collected in the heat exchanger and the wet scrubber. Concentrations of nitrogen- and sulfur-containing organics are not given because they were close or below the detection limit of  $4 \times 10^{-7}$  and  $1 \times 10^{-6}$  wt%, respectively. The contents of the  $\text{NO}_x^-$  and  $\text{SO}_4^{2-}$  inorganic ions were by one to two orders of magnitude smaller than the content of the chloride ions. PVC plastics were used to optimize the combustion chamber operation prior to the start of the test program. Therefore, the facility had become contaminated with products of the PVC combustion prior to carrying the tests, the results of which are shown in Table II. This is indicated by a presence of

TABLE V  
Chemical Composition of Liquids Collected in Heat Exchanger and Wet Scrubber

Test	Inorganic Ions (wt%)		Organic Compounds (wt%)	
	$\text{Cl}^- (\times 10^{-3})$	$\text{F}^- (\times 10^{-6})$	$\text{Cl} (\times 10^{-3})$	$\text{F} (\times 10^{-6})$
Blank <sup>a</sup>	15	31	1.1	12
A	24	470	1.9	18
B	12	420	2.2	15
C	11	390	0.9	19
D	12	400	1.7	14
E	90	540	1.4	22
F	250	620	1.5	21
G	3200	810	1.8	24
H	310	120	1.5	46

<sup>a</sup>In the blank test there was no plastic fed into the combustion chamber. The content of inorganic ions and organic compounds measured in distilled water and fresh absorbate was two orders of magnitude smaller than those observed in the tests.

chlorine in a sample of the blank test when plastics were not fed to the combustion chamber (see Table V). The heat exchanger and the wet scrubber were flushed with acetone before the first test shown in Table II began and then after each test. The acetone washouts prior to the tests also showed the presence of chlorine-containing organics. This confirms that the facility was already contaminated. As can be seen from Table V, starting with test E, during which PVC-containing wastes were fed to the combustion chamber, the concentrations of chloride increased significantly. However, for chlorine-containing organic compounds, no such increase was observed. The contents of organic compounds containing chlorine were on a similar level for the blank test and all the tests independent of the feed composition.

It is also worth mentioning that the presence of fluorine-containing organic compounds, which were not expected to be present in the waste, was observed. Their concentration was on a similar level for all the tests independent of the feed composition. The concentration of fluoride was much above that observed for the blank test. This indicates that fluorine was present in all the plastics combusted, possibly as part of the filler, the plasticizer, or the colored substances added to the plastics during manufacturing for providing specific properties.

The formation of PCDD/PCDF is a common experience in the waste-processing industry for the combustion of materials that contain compounds of chlorine. In this study, the presence of chlorine-containing inorganic and organic compounds in the combustion products of the materials, which were supposed to contain no PVC, indicates that the formation of PCDD/PCDFs should also be expected. The formation of PCDD/PCDFs could occur both in a combustion chamber and during the process gas cooling down. The preferable temperature window for PCDD/PCDF formation is 470 to 670 K. The results of the PCDD/PCDF measurements in liquids collected in the condenser and the wet scrubber and the PCDD/PCDFs remaining in the gas stream after the wet scrubber are given in Table VI. The quantities were on a similar level for all the tests. An increase of the PVC content in the combusted materials would be expected to increase the PCDD/PCDF formation. The results given in Table VI

demonstrate a correlation between the content of PVC in the materials combusted and the quantity of PCDD/PCDFs remaining in the gas stream after the wet scrubber. This also correlates with the quantity of inorganic chlorine ions collected in the wet scrubber (see Table V). The appearance of PCDD/PCDFs in the tests, in which no PVC was used, can be explained by two reasons: Chlorine-containing substances were present in non-PVC plastics, and/or the test facility was already contaminated with chlorine-containing substances outgassing PCDD/PCDFs into the process gas from the combustion of non-PVC plastics. Unfortunately, the aforementioned contamination of the test facility, which occurred prior to the start of the test program, does not allow a conclusion on which of these sources or both of them were responsible for the appearance of PCDD/PCDFs in tests A through D listed in Table VI. As can be seen from Table VI, the wet scrubber was not very effective for removal of PCDD/PCDFs from the process gas. The methodology for the collection of PCDD/PCDFs from the gas phase did not allow estimation of the content of the PCDD/PCDFs that broke through the wet scrubber in a gas state and as sorbed on the solid particles. The results in Table VI demonstrate no apparent effect of the metal presence in the feed on the rate of PCDD/PCDF formation.

#### IV. SUMMARY AND CONCLUSIONS

Materials present in the JET soft housekeeping materials can be decomposed in a self-sustainable combustion process in pure oxygen. A compact combustion facility of scale equal to the facility tested in this study (up to 0.5 kg/h; see Sec. II.B) could provide annual processing of up to 2.6 tonnes/yr of waste on the basis of continuous 24 h/day operation for 220 days. This potentially covers all needs for JET operation. Residual solids will be <8% of the original mass of the processed waste and will contain residual tritium, likely in a quantity smaller than that in the original waste. The solid residues are chemically inactive and consist of mainly metal oxides and carbon and could be disposed of as low-level waste or ILW.

The combustion of waste will result in most of the tritium being released into the stream of gaseous products. Chlorine present in PVC, which is one of the major contributors to the JET soft housekeeping ILW, will also be released into the gas stream. The wet scrubber of a packed type charged with an aqueous solution of sodium carbonate demonstrated effective removal of hydrogen chloride from the process gas. Because the chemical composition of feed waste cannot be predicted, a wet scrubber will need to be charged, independently of actual waste-feed composition, at a rate as for the combustion of pure PVC. In experimental tests the rate of the wet scrubber charging was equivalent to  $\sim 5$  l/kg (PVC). This is in addition to an average rate of water formation, which

TABLE VI  
PCDD/PCDF Yield\*

Test	Amount Collected <sup>a</sup> (ng/kg)		Total Yield (ng/kg)
	In Liquid	In Gas	
A	1.6	1.9	3.5
B	47	6.6	54
C	82	11	93
D	2	2.9	4.9
E	32	200	232
F	51	110	161
G	630	310	940
H	910	1200	2110

\*Yield of PCDD/PCDFs was calculated as equivalent toxicity  $TE$  using measured concentrations  $C$  and toxic equivalency factor  $TEF$  for each individual PCDD/PCDF.  $TE = \sum(C \cdot TEF)$  is a means of expressing the toxicity of a complex mixture of different PCDD/PCDFs in terms of equivalent quantity of 2,3,7,8-TetraCDD.  $TEF$  is based on toxicity of PCDD/PCDF relative to that of 2,3,7,8-TetraCDD, which is universally assigned a  $TEF$  of 1 (Ref. 8).

<sup>a</sup>Quantity of PCDD/PCDFs collected in combined condensate and absorbate liquids and remained in the process gas are given per mass of material combusted.

can be assumed 0.73 kg(H<sub>2</sub>O)/kg(waste). This would result in an effective rate of water generation in the wet scrubber of ~5.7 kg(H<sub>2</sub>O)/kg(waste). Processing 1.5 tonnes/yr of soft housekeeping ILW generated at JET would therefore result in the production of 8.6 tonnes/yr of tritiated water. This is similar to the current rate of tritiated water production at the JET tritium plant.<sup>12</sup> Absorbate produced in the wet scrubber would contain water with a tritium concentration in the range of 9 MBq/kg to 1.2 GBq/kg and mainly carbonate and chloride of sodium. For an average composition of the JET waste, the rate of sodium chloride production can be assumed to be 0.29 kg/kg(waste). To be disposed of the JET facilities or processed, the water would need to be purified from sodium salts. This process would generate solid inorganic salts of sodium, which will contain a small amount of residual tritiated water and, therefore, is likely to fall into the category of LLW.

The process gas purified using a wet scrubber will be chemically inactive and would allow further tritium removal to below the discharge limit employing methods well adopted in tritium technology. Further experimental work will be required to evaluate the process with waste containing tritium.

The results presented in Tables II and VI lead to the conclusion that ~300 ng/m<sup>3</sup> of PCDD/PCDFs will be present in the process gas generated in the combustion chamber of the facility. This is about 3000 times above the limit of 0.1 ng/m<sup>3</sup> specified in the European Union Directive<sup>9</sup> for the exhaust gas of incinerators. According to Table VI, from 12 to 86% of those PCDD/PCDFs would be retained in the process gas after purification in the wet scrubber. To be consistent with the aforementioned directive, a combustion facility for processing the JET soft housekeeping ILW would need to be equipped with an afterburner to improve the combustion effectiveness and with additional process gas purification equipment to remove solid particulate of size <5 μm and equipment for oxidation of halogen-containing organic compounds.

The experimental testing demonstrated that processing plastics, which are supposed to contain no PVC, had however generated toxic halogen-containing organic compounds including PCDD/PCDF.

#### ACKNOWLEDGMENTS

This work was funded by the United Kingdom Nuclear Decommissioning Authority and by the European Communities under the contract of association between EURATOM and

the U.K. Atomic Energy Authority (UKAEA). The views and opinions expressed herein do not necessarily reflect those of the European Commission.

The authors express their gratitude to the Waste Management Group of the UKAEA JET Facilities for assistance in preparation of the materials to be tested. The analysis of the chemical compositions of the liquid and solid products and the PCDD/PCDFs was arranged by I. A. Revelsky, Moscow State University.

#### REFERENCES

1. "Technical Aspects of Deuterium-Tritium Experiments at JET," *Fusion Eng. Des.*, **47**, 107 (1999).
2. A. D. HAIGH, R. MIDDLETON, and G. NEWBERT, "Waste Management Aspects of the DTE1 and RTE Campaigns," *Fusion Eng. Des.*, **47**, 285 (1999).
3. K. E. WILZBACH, *Chem. Eng. News, J. Am. Chem. Soc.*, **79**, 1013 (1957).
4. R. S. DICKSON, "Tritium Interaction with Materials," "CFFTP Basic Tritium Safe Handling Course," Chalk River Laboratories (Oct. 1991).
5. L. BERNSTEIN, "Plastics Contamination with Tritium," Personal Communication.
6. S. KNIPE et al., "Tritium Off-Gassing Trials on Dust and Flakes from the JET MKIIA Divertor," *Fusion Eng. Des.*, **58-59**, 383 (2001).
7. K. Y. WONG, B. HIRCO, R. A. JALBETT, and W. T. SHMAYDA, "Tritium Decontamination of Machine Components and Walls," *Fusion Eng. Des.*, **16**, 159 (1991).
8. R. M. HARRISON, *Pollution: Causes, Effects and Control*, 4th ed., Royal Society of Chemistry (2001).
9. "Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the Incineration of Waste."
10. P. A. SCHWEITZER, "Handbook of Separation Techniques for Chemical Engineers," 3rd ed., McGraw-Hill Book Company (1996).
11. R. S. DICKSON, "Tritium Interactions with Steel and Construction Materials in Fusion Devices," CFFTP G-9039, Canadian Fusion Fuels Technology Projects, AECL 10208, Atomic Energy of Canada Limited (Nov. 1990).
12. A. PEREVEZENTSEV et al., "Conceptual Design of the Water Detritiation Facility for JET," UKAEA Fusion 493, U.K. Atomic Energy Authority (2003).