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Study of JET Soft Housekeeping Waste Volume Reduction by Plasma Arc Centrifuge and Gasification in Countercurrent Regime Methods

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** See annex of F. Romanelli et al, "Overview of JET Results",
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ABSTRACT

A maintenance of the JET reactor led to generation of the soft housekeeping materials contaminated with tritium and comprising various polymeric materials. Some of the wastes fall into a category of intermediate level waste and require a processing. Plasma arc centrifuge and countercurrent regime of gasification have been studied as methods to reduce mass and volume of the wastes. Mass reductions from 8 to 46 have been demonstrated dependent on waste composition. Volume reduction was significantly greater. Analytical procedures for the waste characterization and combustion products have been developed. The wastes and combustion products including chlorine-containing combustion products have been characterized. A formation of water as secondary waste was estimated for countercurrent regime of gasification, which was important for the ultimate processing of tritium-contaminated wastes.

I. INTRODUCTION

JET (Joint European Torus), the world largest tokamak, carried out in 1997 an intensive campaign of operation with tritium, the DTE1 experiment [1], using carbon-Carbon Fiber Composite (CFC) as main plasma facing material. Following maintenance and modification of the machine required handling materials contaminated with tritium. All in-vessel components removed from the vacuum vessel were likely to be contaminated with highly tritiated carbon dust [2]. Therefore, their handling required using protective suits and equipment [3]. Additionally, tents and isolators made of polymers have been commonly employed at JET to control the contamination spreading. As a result, protective suits, equipment, tents, and isolators become contaminated with tritium at level, which often exceed LLW/ILW threshold [4].

Assessment of the JET soft housekeeping ILW stock [4] showed that the tritium concentration varied in the range from 0.05GBq/kg to 7GBq/kg with up to 90% of tritium being “water non-soluble”, i.e., tritium, which does not leach out in a contact with liquid water. “Water non-soluble” tritium can be that chemically bonded to carbon chain of polymers. The tritium distribution in the soft housekeeping ILW was found to be very non-uniform even for wastes collected in the same waste bag. It was assumed that the source of contamination was the carbon dust adhered to the polymeric materials by electrostatic forces. This provides an explanation to the observed contamination of protective equipment with tritium in the form of “hot spots”. A high rate of out-gassing from the dust [2] indicated that tritium was very mobile, and therefore could migrate from the dust to the surface of polymers. However, tritium might further penetrate into bulk of polymers and become chemically bonded [5].

Attempts to estimate an average composition of the JET waste using two sources of information, namely, the data for consumables and records of operations with production of soft ILW, resulted in the following composition of stock of the soft ILW: The JET soft housekeeping ILW includes rubber, cellulose, and three groups of plastics. Plastics consist of polyvinylchloride (PVC), polyurethane (PU) and various plastics of polyethylene type (PE). The PVC group includes 13

different materials, the PU group – 4 materials, and the PE group – 9 materials. Each group of the plastics, cellulose, and rubber constitute substantial fractions of total waste amount and could absorb tritium differently.

Disposal of the JET soft housekeeping Intermediate Level Waste (ILW) would require their long storage until a repository becomes available in the United Kingdom. Due to the low density of polymers and out-gassing with tritium their disposal as ILW, which is costed on the basis of volume, is likely to be an expensive option. A preliminary Best Practical Environmental Option study for JET decommissioning has identified processing such ILW as a preferable option. The objective of the processing should be a recovery of the major part of tritium activity in order to reduce activities of the wastes from ILW to LLW level. Because polyvinyl chloride (PVC) presented a large portion of the JET soft ILW their processing using non-destructive methods was considered to be the most preferable option.

Preliminary study of non-destructive methods included ultrasonic cleaning as the method commonly adopted in nuclear industry. Different surfactants of TechXtract type were used in the trial. The experimental procedure included overnight soaking of the JET wastes in mixture of surfactants followed by sequence of ultrasonic bathing in their various mixtures. Small tritium recovery fraction, on a level of a few percent only, was observed.

Next experimental trial was to test thermal desorption, a partially destructive method. Reactor filled with samples of the JET waste was purged with either wet or dry inert gas while being heated to temperature of 620K at the rate of 50K/h. After exposure of samples to temperature of 620K for 3 hours, the reactor was further heated to 770K and maintained at this temperature for another 3 hours. Tritium released from samples in the form of water vapor was collected in water bubblers connected in series. Tritium as gaseous hydrogen was catalytically oxidized. Tritium captured in the water bubblers, remaining in ash and solid particulates were measured. Fraction of tritium released was found to be about 50% for both purges with wet and dry gases. Partial decomposition of plastics, possibly due to pyrolysis, started at temperature around 500K and finally resulted in about 40% to 50% mass loss with formation of gaseous and liquid products. The thermal desorption method did not result in a considerable detritiation of waste but presented a need for processing tritiated gaseous and liquid products produced during the plastics decomposition.

Tests described above demonstrated that detritiation of the JET soft housekeeping waste from ILW to LLW level was difficult to achieve. Therefore, efforts were re-directed towards achieving a considerable waste volume reduction to reduce the cost of the waste disposal.

Development of a method for the detritiation of the JET soft housekeeping ILW requires a proof of the technique's effectiveness in processing materials contaminated with tritium. It was decided to prepare polymers contaminated with tritium, measure tritium inventory and distribution, and use them as samples for decontaminations tests.

Among several procedures [6-8] of materials' loading with tritium most effective is the method

reported by Wilzbach [7]. The procedure includes an exposure of materials to gaseous hydrogen, which contains tritium.

Polymeric materials were exposed to gaseous hydrogen, which contained 40 at% tritium, at room temperature and gas pressure of 0.05 MPa. The samples were placed in the reactor such a way to make all the surfaces accessible for tritium. The variable parameter was the exposure duration.

Analysis of tritium content and distribution in the waste samples exposed to tritium was carried out by using three different techniques: First was a complete combustion of the waste sample at temperature of 1070 K in air followed by collection of released gaseous tritium in a sequence of water bubblers. Second method was based on leaching a sample in water for one month followed by a complete combustion of the sample as described above. This technique, adopted at JET for soft waste characterization, allowed distinguishing between “water-soluble” (which was assigned to tritium not chemically bonded to polymers) and “water non-soluble” tritium. The last method used radioluminography (RLG) [9] for analysis of tritium distribution along the surface exposed to tritium and tritium depth distribution in the material.

Table I compares results of tritium measurements in various materials exposed to tritium for 1 hour. Complete combustion, which is commonly used in tritium facilities, gives tritium activity for most of the samples significantly lower than two other techniques. This discrepancy can only be explained by imperfection of the former method that systematically underestimates tritium content in polymeric samples. Significant portion of tritium in the studied polymers exposed to the hydrogen-tritium mixture was in a “water-soluble” form. This tritium originated from tritium-containing hydrogen molecules diffused in the pores of the polymeric material and physically adsorbed on the surfaces.

Table I also shows that a large fraction of the tritium inventory in the plastics was in a water non-soluble form. Plastics of polyethylene/polypropylene and polyvinylchloride groups, which contribute mostly to the stock of JET soft housekeeping ILW, contain a large portion of chemically bonded tritium. This helps to explain why non-destructive methods were unsuccessful in recovery of tritium. The fraction of water non-soluble tritium in rubber, polyurethane, and cellulose was significantly smaller than that in the plastics of PE and PVC groups. Cellulose, whose content in the JET soft housekeeping ILW is lower than that of plastics of PE and PVC groups, nevertheless, can be a large contributor to tritium inventory of that waste because cellulose takes up substantially more tritium than the other polymers.

Table II shows the tritium concentrations, measured using the RLG method, on surface of the materials of PVC and PE groups exposed to tritium for varied time. The different materials of the same waste group showed significantly different tritium contents, which differed by about an order of magnitude. There was no linear correlation between tritium content in materials and duration of their exposure to tritium.

Tritium depth distributions in the polymeric materials evaluated using RLG method by measuring tritium distribution on the surfaces produced by cutting samples across show a uniform tritium

distribution across the polymeric materials, as illustrated in Fig.1a. This might result from easy tritium penetration through polymeric materials due to their well-developed porous structure. When the polymeric materials contained reinforcing fibers, tritium preferably retained around these fibers. This is clearly seen in comparison of Figs.1a and. 1b, which show the tritium depth profiles for a sample of PVC sheet reinforced with nylon fibers.The sample was cut either between the fibers (Fig.1a) or across a fiber (Fig.1b). Tritium distribution along the surface exposed to tritium in Fig. 1c shows location of a fiber coming close to the surface analyzed.

The above review allows one to draw the following conclusions.

- a) Processing of JET soft ILW can be successful applying a complete decomposition.
- b) The methods for soft ILW decomposition should reduce tritium contained in the waste to a form, which can be readily recovered and provide processing to recover or concentrate tritium and/or safe and compact waste storage.
- c) Mass or volume reduction factor shall be used as a measure for efficiency of JET soft ILW processing.
- d) The processing should produce a minimum amount of secondary radioactive or chemical pollution.

A review and analysis of options based on the effectiveness, operability, and safety together with simplicity to implement into the JET environment led to selection of three waste treatment methods for experimental trials: self-sustainable combustion in pure oxygen, plasma arc centrifuge, and gasification in countercurrent regime with further combustion of the gas. All these methods are aimed at achieving complete oxidation of the organic part of JET soft ILW, so as to transfer tritium to water produced in oxidation. This approach is based on the knowledge that tritiated water vapors can be recovered from a gas stream of combustion products and that processing of tritiated water to recover tritium therefrom is a problem, which has a known solution. Then, if only the solid residue of processing comprises residual ILW/LLW, the volume and mass reduction attainable is high.

Trial of the first of three methods is described in ref. [4]. This paper deals with the second and third ones.

2. WASTE COMBUSTION IN PLASMA ARC CENTRIFUGE AND GASIFICATION IN COUNTERCURRENT REGIME

2.1. MATERIALS TESTED

This study was devoted to a treatment of the JET soft housekeeping wastes by using plasma arc centrifuge combustion and countercurrent gasification. As a first step of the study, all the experiments were carried out with in-active model JET wastes. The materials tested were already described in Introduction and specified in Table I.

The JET soft household waste is quite variable in its chemical composition. However, major

constituents are combustible polymeric materials. Those include polyethylene and polypropylene of general formula $(CH_2)_x$, cellulose $(C_6H_{10}O_5)_x$, PET $(C_6H_{10}O_5)_x$ and other plastics. A substantial part of JET ILW comprises PVC materials, mostly in the form of flexible films of extended PVC, some of them nylon-reinforced. The chemical composition of samples tested is given in Table III. The analyses were performed on six samples of PVC materials, two samples of PU, and one rubber sample. One can see that even within one group of materials (PVC) different items substantially varied in chemical composition and ash content.

An objective of the study was to test tolerance of a processing method to variations in waste composition. Therefore, the tests were performed on varied combinations of the materials comprising JET ILW. A sample of mixed plastics MX was formed as a mixture of rubber, polyethylene, polyvinyl, polyester, polypropylene. A concept to use the same samples for all experiments based on two combustion methods was accepted. The JET soft housekeeping wastes were shredded to 10x10 mm size. The waste compositions studied are specified in Table IV. Considering that the JET wastes could have in its composition various metals and their concentrations in the wastes could significantly differ, the decision was made to add 2% mass of metals (aluminum and copper foils and shavings of stainless steel) to the wastes being investigated. An addition of metals to the JET soft housekeeping wastes provided a possibility to reproduce possible variation of JET wastes and to understand how these two destruction methods would be dealing with these wastes ingredients.

2.2 DESCRIPTION OF PROCESS FLOW DIAGRAM AND OPERATION PARAMETERS

2.2.1 Gasification in countercurrent regime

Process flow diagram is shown in Fig. 2. Gasification tests were performed in a cylindrical batched reactor

1 with a refractory tube made of fused quartz. The quartz tube had total length of 1000mm; inner diameter was 160mm, tube wall was 4mm thick. The tube was provided with five thermocouples **4** placed at outer surface to measure temperature profiles along the reactor.

The lower part of the reactor was used to ignite the waste studied. The ignition part included ignition fuel and electric heater **3**. The ignition fuel (20g of wood shavings and 50g of charcoal) was placed in the reactor onto the lower grating. An experimental run was started with energizing the heater and start of air supply **2**; the air heated to approximately 400°C ignited the ignition fuel.

The main part of the reactor, 1000mm long cylinder, was filled with the material gasified in a mixture with 30 – 40mm mesh size pieces of solid inert material (SiC). To reduce radiation heat loss, the quartz refractory tube **7** was supplemented with a polished aluminum mirror screen within the walls of stainless steel outer shell. Following the ignition, the combustion zone formed and further propagated upward over the charge of the material gasified. The pyrolysis zone propagated ahead of the combustion zone.

Sampling of gaseous products of gasification **8** was done from the upper lid of the reactor. Adjacent to the reactor was afterburner **10**, wherein aftercombustion of the product gas, which

included gaseous products of char combustion and volatiles released in pyrolysis, was arranged. The aftercombustion secondary air **9** was supplied to afterburner. Combustion of the product gas was ignited with electric heater **11**. The supply of gasification air and aftercombustion air was controlled with flow meters not shown on the drawing.

To humidify the gasifying agent, the steam from the steam generator not shown on the drawing could be directly supplied into the gasification air feed line. Steam supply rate was controlled through the current in the electric heater of the steam generator. Generally, water is used as an endothermic oxidant that provides means for temperature control and enhances product gas calorificity through water-gas reaction $\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$. In the preliminary experiments for gasification of the soft housekeeping wastes, the steam was occasionally used to control the combustion temperature, when the latter became excessively high. It was our understanding that introduction of any additional water to the process was undesirable, since it would cause excessive amounts of tritiated water that will require further processing. Therefore, steam was not supplied during actual tests, while a possibility to supply it was an additional control means.

The product gas from the gasifier reactor was sampled for further analyses of under-mass-44 species using a mass spectrometer and then was burned with the supply of secondary air in the afterburner provided with an electric heater. Propane gas **12** was additionally supplied to the afterburner. The supply of the propane was necessary as the preliminary experiments showed that aftercombustion even with fully energized electric heater of the afterburner failed to secure sufficient oxidation of the product gas on the final stage of the process, when residual char was burned in the gasifier and the product gas was practically incombustible even with additional heating. Concentration of CO in exhaust gas on the final stage in those preliminary experiments exceeded measurement level of the gas analyzer (2000ppm).

Further, the exhaust gas was sampled from within the afterburner for concentration of oxygen, carbon monoxide, sulfur dioxide, nitrogen oxide, and nitrogen dioxide measured using a *Kane-May* Quintox KM-9006 gas analyzer with electrochemical sensors for these gases. When processing mixture contained PVC, the probing gas flow was bubbled through a sodium carbonate solution in order to protect the analyzer from the hydrogen chloride formed in the process.

The exhaust gas flow from the afterburner was then passed through condenser **15** cooled with tap water **16** (10°C) and further directed into a packed absorber **18** with the packing (*18Kh10NT* stainless steel 2×2 Levin spirals) irrigated with sodium carbonate solution **19**.

The exhaust gas flow from absorber **19** was pumped through filter **21** to recover polychlorinated dibenzodioxins/dibenzofurans (PCDD/PCDF) that passed through the condenser/absorber cleansing system. Further, the filter was analyzed for PCDD/PCDF. The power of the exhaust fan **22** was controlled to maintain the pressure within the afterburner close to atmospheric one.

The sodium carbonate used to prepare solutions was of *analytically pure* grade (content of chlorides, sulfates, and nitrates within 0.001%, 0.0025%, and 0.004%, respectively). The condensate from condenser **15** and spent solution from absorber **18** were collected after each experiment and

analyzed for particulates, pH, content of Hal-, S-, and N-containing organics, and anions.

There was a possibility that some chemical compounds could be deposited in the absorber. Therefore, it was decided that between all experiments the absorber was washed out with 1 L of acetic acid and then twice with 1 L of acetone to clean the system for the next experiment. Acetone as a washout liquid was selected because it was assumed that water-soluble chemicals were already washed out. The necessity to wash the absorber with acetic acid additionally brought about the spent acetic acid solutions, which also could contain the chloroorganics under check.

Upon consumption of the processing mixture (indicated by the temperature at the gasifier outlet passing through a maximum), the primary air supply was continued for approximately 20min to provide burnout of the char residue in the gasifier, while the flame in the afterburner was supported by the propane supply and electric heater. Further, air supply was stopped and gasifier cooled. Upon complete cooling of the gasifier, the solid residue was discharged and the solid inert material was handpicked from it. A single stock of solid inert material was recycled and used in all tests. No special care was taken to clean the solid inert of ash particles stuck to its surface, so a small fraction of ash could be transferred from one experiment to another.

Whenever the solid residue contained a noticeable fraction of unburned char, the latter was determined by mass loss during calcining for 30 min at 600°C in air. The residue left after calcining is called further residual ash. Mineral composition of the residual ash was determined using atom absorption/emission spectroscopy.

2.2.2. Plasma arc centrifuge

The Plasma Arc Centrifuge (PAC) is a main element of the laboratory facility developed to treat the soft housekeeping wastes. The waste treatment was envisioned through plasma-assisted combustion of the waste in a controlled atmosphere. The facility was equipped with a plasmatron, metering unit, a system for gas sampling, and a system to deliver gaseous streams (air and oxidant gas).

Schematic process flow diagram for a PAC system to treat tritium-contaminated soft housekeeping wastes is given in Fig.3. The system had hermetic chamber **1** equipped with a subsystem to provide vacuum, another subsystem to create controlled atmosphere, source of plasma arc feeding, a subsystem to ignite and control the plasma, devices and instrumentations to monitor and control process (they are not shown in the process flow diagram) and gas pump **2**. During operation of the system, vacuum and a forced flow of air or another oxidative gas were set up in chamber **1** by gas pump **2** located at the outlet of gas system before a ventilation system (not shown in Fig.3).

The soft housekeeping materials were placed into metering unit **3** that was arranged on top of chamber **1**. Delivery of materials into fast rotating crucible **7** was carried out from metering unit **3** through materials feeding pipe **16** cooled with water. A waste feeding rate was determined by the rotation rate of the metering unit and volume of materials in single transfer scoop of the metering unit. The volume of the single portion was determined by the scoop's size. When the metering unit worked, the materials were delivered into mixing chamber **4** where they were mixed with an air (or

any other oxidative gas) flow supplied through flow meter **5** and control valve **18**, which, respectively, monitored and controlled the gas flow rate. An additional quantity of oxidative gas was necessary to provide its excess and guarantee complete materials combustion in hermetic chamber **1**. Plasmatron **6** of METCO type with elongated cases to input a plasma jet into working space of crucible and with capability to moving up and down was also attached atop chamber **1**. Rotation of crucible **7** was achieved with an actuator installed beneath and outside the chamber and along the chamber axis. The rotating drive shaft entered the chamber through vacuum seals. Crucible was made of copper with its internal surfaces covered with a layer of corrosion resistant high calcitrant ceramics to enhance efficiency of the process; the plasma volume was cooled down with water. As a refractory liner to cover lateral groove surfaces of the crucible, 5-8mm-thick aluminum oxide was used. A 15-mm-thick aluminum oxide ring covered the bottom of the crucible. Chamber **1** was equipped with thermocouples providing measurement of the temperature in different parts of the chamber.

Gaseous combustion products from chamber **1** passed through two-stage pipe-in-pipe condenser **9**. The first stage of condenser **9** was used to cool the gas stream to 100-150°C to collect gas samples and the second one, to estimate concentration of water vapor in the gas through measuring liquid water volume formed by condensation of water vapor. Upon water vapor condensation in the condenser, the water absorbed hydrogen chloride forming hydrochloric acid solution collected in vessel **12**. Uncondensed gas stream was directed to bubbler **10** where gaseous hydrogen chloride had been dissolved and neutralized by aqueous solution of sodium carbonate (the bubbler's charge delivered there from vessel **11**) with formation of sodium chloride. Gases and particulates breaking through the bubbler were passed through packing filter **13**, which worked as a demister preventing entrainment of liquid to a vacuum pump.

3. APPROACH TO EXPERIMENTS

The waste combustion in PAC and gasification in countercurrent regime required different approaches for preliminary experiments with individual wastes. The PAC experiments required carrying out blank experiments only to ensure that auxiliary equipment works properly. The gasification experiments with individual wastes and some mixtures of the wastes required understanding of the wastes behavior during combustion. They also allowed finding optimal parameters for the final experiments.

The goal of the final experiments was to obtain parameters for a future comparison of two competitive primary methods to destroy the soft housekeeping materials. This means that analytical procedures used for both primary destruction methods had to be similar.

During the final experiments, it was necessary to obtain not only the results of waste destruction but also make an estimate for corrosive characteristics of various materials that could be used for construction of apparatus if one or both of these methods were selected for a future application. In order to obtain the characteristics, a number of samples for various possible construction materials

was put at different locations inside the combustion system for final tests. After all final tests the samples were removed and examined to determine whether they suffered corrosion. Additionally to that, the structural materials used to make the experimental installations themselves and sampling instruments unavoidably underwent tests for their corrosive resistance. However, the results of corrosive testing are not a part of this publication.

The comparison of two different methods to destroy wastes can be done based on the following parameters:

- Extent of reducing waste mass and volume;
- Composition of combustion products formed including gases, liquids, and/or solids;
- Composition of ash remaining after combustion;
- A necessary purification system to treat combustion products;
- Reliability of control;
- Tolerance to variation in the composition of the waste processed.

It was our intent to obtain as much information as possible within the frame of the research. Especial attention was given to mass and volume reductions achieved in these experiments. Mass of the waste feeding to the Plasma Arc Centrifuge (PAC) and a gasifying reactor and residual ash remaining after combustion were determined when it was possible. The residual ash remaining after combustion was divided into two halves. One part of the collected residual ash was analyzed using atomic emission analysis in order to obtain concentrations of main metals in the ash composition. The second part of the ash was put into 20mL of deionized water to determine pH of the formed solution and the concentration of chloride anion in this solution by titrating with mercury (II) nitrate. The 20 mL volume was selected as a minimum quantity of water to use a pH-meter. The information about pH of the solution gave an understanding about the reactivity of the remaining ash, which considering a possible presence of tritium in the ash residue of treatment of tritium-containing wastes, has to be stored in a storage due to the possible ash radioactivity. If the pH of the solution formed by placing the ash remaining after combustion into water were acidic, the materials used for ash storage have to be resistant to corrosion. A presence of chloride in the ash can lead to an additional requirement to a sealing of storage vessels because humidity from the air can cause a chemical reaction with a formation of hydrogen chloride with respective consequences.

In all experiments, condensed water was collected and its volume measured to obtain information about water vapor concentration in the gas phase. This information was necessary for the future research of tritium-containing wastes.

Considering that Cl-containing PVC combustion products could contaminate the whole system, experiments without PVC were carried out in a first turn, and then the experiments with PVC. Between all experiments with PVC an absorber was washed with acetone to clean the system prior to the next experiment. In order to have blank samples, the absorber was washed out with acetone

and then with sodium carbonate solution before the first experiment.

The sodium carbonate solution was used as a charge for a bubbler applied in the PAC and an absorber charge in gasification experiments. The concentration of these charges was determined before the experiments and the spent charge volumes and their pH value was measured after the experiments. A condensate after the condenser was mixed with the spent absorber/bubbler charge. This allowed extracting all condensed combustion products including entrained solid and liquid particles from the gas exhaust. Design of air pollution control system was not a goal of this research; the design of this system was done in a way to obtain maximum information for identifying the composition of combustion products; nevertheless, this approach, which was proven operative, could be used in a pilot plant as a future purification system for cleaning exhaust. Considering that the goal of the research was to obtain comparative information for two primary destruction methods, even not the optimal design gave us sufficient information for purposes of comparison.

The mixed solution was divided into two parts. The first part of the solution was filtrated to mechanically trap solid particles on a filter. The filter also extracted PCDD/PCDF from the liquid phase. Further the filter was used for determining possible PCDD/PCDF content.

The second part of the solution was also filtrated and the concentrations of halogen-containing organic compounds and inorganic anions were determined in the filtrated solution. Inorganic anions can characterize a formation of “acid” gases during waste combustion and allow estimating “acid” gases concentrations in gas phase.

Solid particles left on the filter after filtration of the second part of the solution were used to estimate their mass and size distribution. It is understood that the size distribution will not be exactly equal to the one for particles in gas phase but at least it gave us an idea about the size range.

The exhaust gas after absorber in gasification in countercurrent regime and after bubbler/demister in plasma arc centrifuge was pumped through a fine quartz filter impregnated with stationary phase and layer of polymer sorbent XAD 2 to recover polychlorinated dibenzodioxins/dibenzofurans (PCDD/PCDF) that broke through the condenser/absorber cleansing system.

2.4. ANALYTICAL PROCEDURES

2.4.1. Inorganic Anions Determination in Spent Soda Solutions from Absorber

Inorganic anion determinations were performed using Ion Chromatograph (IC) with conductometric detector. Two-columns mode was used. A PCC 1HC (12.5×4.0mm) and Star-Ion-A300 (100×4.60mm) columns were used for preliminary concentration of chemical compounds and for their separation, respectively.

A mixture of 3.60μM NaHCO₃/3.75μM Na₂CO₃ with flow rate of 1.0μL/min was used as eluent.

100-10000 times dilution with deionized water was used depending on a sample. The 20μL samples were injected into IC using sampling valve. Impurities content was calculated as peaks area, taking into consideration dilution and injected sample volume. Solutions with known anion concentrations (5×10^{-10} – 5×10^{-5} g/μL) were used as reference. Three parallel analyses were performed

for each sample.

Table V shows the detection limit in optimum conditions for the anions of interests. The relative standard deviation at 1-ng level was no more than 4%.

2.4.2. Total Halogen, Sulfur-, and Nitrogen-Containing Organic Compounds Determination in Spent Soda Solutions and Acetone Washouts from Absorber

2.4.2.1. Total Halogen-, and Sulfur—Containing Organic Compounds

Determination of organic compounds was carried out by using high temperature oven, flow quartz reactor with removable collector at the outlet, and ion chromatograph with conductometric detector. A PCC 1 HC (12.5×4.0mm) and Star-Ion-A300 (100×4.60mm) columns were used for preliminary concentration of chemical compounds and for their separation, respectively. Separation conditions in the columns were the same as described in Chapter 2.4.1. 1 mL of the soda solution was transferred into a micro-extractor where 300 mL of isooctane were added to carry out an extraction.

Extract was collected using a syringe and injected into a quartz reactor with continuous oxygen flow. Oven temperature was 1000°. The sample volume was 1-3 µL. Oxygen flow rate was about 20 µL/min. The collector at the reactor outlet was filled with 5 µL of deionized water. Time of samples decomposition and exhaust collection was 5-7 min. The samples from collector were injected into IC using metering valve. Anions content was calculated as peaks area, taking into consideration the absorbing solution volume in the collector, the injected sample volume and the extraction solvent volume. Solutions with known halogen-containing compound concentrations in methanol (10^{-9} - 10^{-6} g/µL) were used as reference. Three parallel analyses were performed for each sample. The relative standard deviation for this concentration level was no more than 8%.

Acetone washouts were analyzed using the same technique excluding the extraction procedure.

2.4.2.2. Total Nitrogen-Containing Organic Compounds

1 ml of dichloromethane was added to 15 ml of water solution to be analyzed. This mixture was intensively shaken for 5 minutes, and then the organic layer (extract) was collected into a 2 ml vial. The remaining water solution was acidified to pH≈2, mixed again with 1 ml of dichloromethane, and shaken for 5 minutes. This second organic extract was separated from the water solution and was mixed with the first extract after transfer into the same 2 ml vial. This vial was placed into GC-AED auto sampler for the analysis.

The following GC-AED conditions were applied:

- Inlet: splitless, purge flow - 10 ml/min, purge time - 1.0 min, gas saver - 17 ml/min: 2 min;
- Column: HP-100% Methyl Siloxane, i.d. - 250 µm, film thickness - 0.25 µm, length - 30 m;
- carrier gas: He;
- Flow rate: 1.2 ml/min;
- Reagent gases: oxygen at 98595 Pa (14.3 psi), hydrogen at 59295 Pa (8.6 psi)

- Solvent vent on: 1.7-3.7min;
- Programmed temperature: 40°C (2 min); 20°C/min up to 250°C, 250°C (40 min);
- Simultaneous detection of C and N responses (at 193 and 174 nm, respectively);
- Injected volume: 1µl.

5.05×10^{-9} g/µl solution of trifluraline ($C_{13}H_{16}F_3N_3O_4$) was used as a standard for nitrogen content calculation. Peak area of trifluraline at nitrogen channel was compared to the sum of nitrogen peak areas obtained for the respective extract, and then the nitrogen content in the injected volume was calculated as proportional to nitrogen content in trifluraline.

II.4.3. Polychlorinated Dibenzodioxin/Furans Determination

II.4.3.1 Sampling Procedures

Gas phase of waste combustion products to determine PCDD/PCDF was collected using a *TFIA-2* Staplex aspirator supplied with a filter holder (diameter 200mm, ~100µL volume), which was connected to the absorber outlet. Gas phase was pumped through aerosol filter (20µm-thick, diameter 200mm) made of Ultrathin Fiber Quartz (UFQ) impregnated with stationary phase and layer of polymer sorbent XAD 2. Before the sampling, filter and polymeric sorbent were spiked with a standard PCDD/PCDF $^{13}C_{12}$ -labeled mixture. After the sampling, the filter holder was disconnected from the absorber and filter and sorbent were removed from the holder and placed into polyethylene bag for transportation and storage.

Glass bottles for water samples were washed by water with detergent, clean water, distilled water, acetone and then silanized by trimethylchlorsilane.

2.4.3.2. PCDD/PCDF Transfer into Organic Solvents

Transfer of PCDD/PCDF from the filter and sorbent was carried out using Accelerated Solvent Extraction (ASE), which was a liquid extraction at elevated pressure and temperature.

The filter and polymeric sorbent after gas sampling were grinded together, placed in the extraction cell to transfer PCDD/PCDF into the organic phase. The extraction was carried out with 700µL of toluene/acetone mixture (9:1 by volume) at 95-98°C. The extract was evaporated to 0.5-1-ml volume by using a rotor evaporator.

The liquid sample, which could also contain entrained solid particles, was formed by pumping the gas of the waste combustion through a bubbling trap liquid or absorber charge. The liquid samples were thoroughly mixed to distribute solid particles and aliquot of 2-3L was taken for extraction. The aliquot solution was spiked with a standard PCDD/PCDF $^{13}C_{12}$ -labeled mixture.

To recover PCDD/PCDF from the liquid sample, the Solid Phase Extraction (SPE) was applied to the sample. Ultra thin quartz wool impregnated with a chromatographic stationary phase was used for SPE. The diameter of the SPE filter was about 10 cm and thickness of the filter was about 1cm. The flow rate of the liquid sample through the SPE filter was about 3L/hour. After liquid

filtration through the SPE filter that allowed removing solid particles and PCDD/PCDF extraction from the liquid sample, the SPE filter was dried and ASE was applied to transfer PCDD/PCDF, that were sorbed on the SPE filter and on mechanically trapped particles, into an organic phase. A volume of 150mL of toluene/acetone mixture (9:1) was used for PCDD/PCDF extraction from the SPE filter.

2.4.3.3. PCDD/PCDF Isolation Procedures

The extracts obtained had to be purified to isolate PCDD/PCDF for their GC/MS determination. The isolation procedure had several steps.

At first, the purification was performed using a “multilayered” glass column **1** (500mm x 25mm). Column **1** was filled up consecutively with glass wool, 10 \dagger cm³ of neutral silica gel, 10 \dagger cm³ of silica gel impregnated with hydroxides of potassium and cesium, 10 \dagger cm³ of sodium sulfate, 10 \dagger cm³ of silica gel impregnated with sulfuric acid, 10 \dagger cm³ of sodium sulfate, 10 \dagger cm³ impregnated with hydroxides of potassium and cesium and 10 \dagger cm³ of neutral silica gel.

The extract solution was passed through Column **1** to remove acids, alkalis, traces of fats and other compounds with various functional groups. Column **1** was washed out with 200mL of 1:1 hexane/methylene chloride mixture. The eluate was designated as Product **1**.

Product **1** after Column **1** was passed through glass column **2** (50mm x 3mm) filled up with glass wool and mixture of activated charcoal of FAS-MD grade with zeolite (1:10). The Product **1** flow rate through column **2** was about 2 \dagger mL/min. PCDD/PCDFs were retained on the charcoal. Then column **2** was washed out with 20 \dagger mL of hexane/acetone mixture in 1:1 ratio (flow rate ca. 2 \dagger mL/min) and the whole solvent volume passed through column **2** was discarded. Then outlet of Column **2** was connected to a flask containing toluene and PCDD/PCDFs were eluted from Column **2** by reverse toluene flow (2mL/min flow rate). This eluate was labeled Product **2**.

Product **2** was diluted with 45 \dagger mL of hexane and additionally purified using glass column **3** (200mm \times 14mm) filled consecutively with glass wool, 1cm³ of neutral silica gel, 1cm³ of silica gel impregnated with hydroxides of potassium and cesium, 1cm³ of sodium sulfate, 1cm³ of silica gel impregnated with sulfuric acid, 1cm³ of sodium sulfate, 1cm³ impregnated with hydroxides of potassium and cesium and 1cm³ of neutral silica gel. Product **2** going through Column **3** was purified of polar compounds that left in Column **3**. The eluate from Column **3**, free of polar compounds, contained PCDD/PCDF. To guarantee that maximum PCDD/PCDF were washed out from Column **3**, the latter was additionally washed out with 50mL of hexane and then purged by nitrogen flow to remove the solvent from the sorbent pores. This combined eluate was labeled Product **3**.

Product **3** was passed through glass Column **4** (150mm \times 10mm) filled with glass wool, 4g of aluminum oxide, and 2cm³ of sodium sulfate. Then, Column **4** was washed out with 30mL of hexane (this eluate was discarded), 40mL of hexane/methylene chloride mixture in a 19:1 ratio (this eluate is usually used for PCB determination but in this analysis was discarded) and 50mL of hexane/methylene chloride mixture in a 1:1ratio (this eluate is used for PCDD/PCDF determination,

and was designated as Product 4). Product 4 was evaporated to 2mL in a Kuderna-Danish apparatus; the solution obtained was transferred into a 2mL vial; then 1ng of recovery standard - 2-fluoro-6,7,8,9-TCDD in 50mL of acetone and 10mL of tridecane were added to the vial. The prepared solution was evaporated under nitrogen flow to 10mL. 1mL of the final extract was injected into chromato-mass-spectrometer.

2.4.3.4. GC/MS Determination of PCDD/PCDF

Determination of PCDD/PCDF was carried out using a Varian 3400 gas chromatograph and a high-resolution Finnigan MAT†95XL mass-spectrometer. Separation of PCDD/PCDF was performed using DB-5MS capillary column (length - 20m, i.d. 0.2mm, stationary phase film thickness - 0.18mm). Conditions of chromato-mass-spectrometric analysis were the following:

- Injector temperature – 270°C;
- Interface temperature – 270°C;
- Initial column temperature – 140°C (hold 1 min);
- Temperature program – 14°C/min up to 240°C; 3°C/min up to 270°C;
- Temperature program – 3°C/min up to 270°C;
- Final column temperature – 270°C (hold 20 min);
- Electron impact ionization 74eV;
- Emission current 1mA;
- Scan time 0.5 sec/scan;
- Sample volume – 1ml;
- Resolving power – 10,000.

The identification of PCDD/PCDF in the final extract solution was carried out before quantification. To provide reliable identification, two criteria were used: match in relative retention times for sample components and their standards and match in corresponding ratios of characteristic ion mass peak areas (M_1/M_2). These ratios should fall within $\pm 15\%$ of respective theoretical values. Masses (m/z) of characteristic ions corresponding to target PCDD/PCDF and internal standard-surrogates are given in table†VI.

Analysis of standard solution was performed every 12 hours between analyses of the samples.

Quantitative data processing was performed by means of isotopic dilution and internal standard method using response factor values. Internal standards had physicochemical properties and retention times close to the ones of investigated compounds. Five internal standards specified in Table VI were used for all compounds.

Calibration curve was constructed by analyzing standard solutions obtained by dilution of stock standard solutions supplied by Cambridge Isotope Laboratory with concentrations from 10 to 1000pg/ml depending on a component. Calculation of response factors with respect to $^{13}\text{C}_{12}$ -2,3,7,8-tetraCDD was carried out using peak areas registered in the chromatograms for one of respective

characteristic isotope ions corresponding to target compound and internal standard. In order to check initial calibrating curve, a solution of target PCDD/PCDF (including all internal standards-surrogates) with a mean concentration level was analyzed every 12 hours. The retention times of internal standard-surrogates and their response factors were estimated after data acquisition using analysis of calibrating control standards.

To monitor the accuracy of quantitative analysis the following were performed:

- Routine verification of calibration curve stability;
- Determination of relative retention times windows;
- Blank analyses;
- Routine verification of chromato-mass-spectrometer hardware tuning by analyzing perfluorokerosene.

PCDD/F masses determined as a result of analysis were converted in concentrations in gas or water by dividing the masses by sample volumes. A relative standard deviation for PCDD/PCDF determination was within 30%.

2.4.4. ATOMIC ABSORPTION/EMISSION ANALYSIS OF ASH

An ash sample of 0.4-0.6g was placed into a Teflon box with a cover, and the box was placed into a stainless steel hermetic bomb; 5 mL of chlorazotic acid and 2mL of concentrated hydrochloric acid were poured into the Teflon box with the ash. The bomb was exposed to 200°C for 2 hours. After cooling, the bomb was opened and the Teflon box content was transferred to a paper filter, which was preliminary dried to a constant mass at 105°C temperature and weighted. The filter was washed with bidistilled water until filtrate volume was 50mL. The filtrate was used to determine cadmium by atomic absorption spectrometry in air-acetylene flame by using a Hitachi spectrometer with Zeeman effect, and other elements in filtrate were determined using inductively couple plasma method with a Polivac E1000 spectrometer. The filter with residual solids was dried to a constant mass at 105°C and weighted.

3. RESULTS AND DISCUSSIONS

3.1. GASIFICATION IN COUNTERCURRENT REGIME

For all tested compositions of the wastes a similar procedure was followed. The gasifier reactor was charged with an ignition mixture (20g of wood shavings and 50g of charcoal). Further, a waste material (standard 10mm mesh fraction) as a mixture with solid inert material (SiC, 20 – 40mm size pieces) with a 1:4 mass ratio was charged into the gasifier reactor. An additional 500g load of solid inert material was also placed onto the waste charge.

Seventy two (72) gram of the metals was introduced in processing mixtures in Experiments 6, 8, 10: aluminum foil (20g per 1kg of the waste processed), copper foil (20g/kg), and stainless steel shavings (20g/kg).

Table VII summarizes experimental conditions and the main results for all the Countercurrent Gasification (CG) experiments.

In some experiments the solid residue after combustion in gasifier contained a noticeable fraction of unburned char from some of the wastes. In those cases, in order to determine the content of carbon, the residue was heated in air to 600°C for 30 min. Upon visually complete char oxidation, the remaining ash was cooled down and weighted. The pieces of metals if they were in the solid residue were removed from the ash. This ash remaining upon calcining and picking out metal pieces hereinafter is called residual ash. Note that the residual ash was quite fluffy and any further manipulation such as weighting, separation of samples for analyses, etc. resulted in its noticeable compaction. Therefore, the ultimate densities of the residual ash will be lower than those reported in Table VIII.

A presence of unburned char in the ash was not an unavoidable feature of the gasification process. Rather, it revealed a poor heat insulation of the gasifier reactor. Indeed, the analytical procedure used to determine char content prompted that a better heat insulation and/or implementation of an additional heater would secure for the ash residue a residence time sufficient for complete burnout of char at high temperature.

The properties and compositions of the solid residue of gasification are summarized in Table VIII.

The metals (metal pieces present as an admixture in PU sample and those intentionally introduced in the processing mixture in Experiments 6, 8, and 10) generally preserved their identity. However, aluminum foil was partially melted and underwent noticeable oxidation. Pieces of copper foil and stainless steel shavings also strongly corroded under processing conditions. This noticeable oxidation of metals was also revealed by the mass of metals from the solid residue (the mass of the 3mm+ fraction of the solid residue was assigned to metals) being greater than the mass of the metals charged.

Table VIII also shows the results of calculated estimates for metals content in the housekeeping waste based on the atomic spectrometry experimental data of metals determination in the residual ash.

As can be seen from Table VII, two experiments with PVC (8 and 11) and four experiments (5, 6, 9, and 10) with the mixture of the individual wastes can be considered as parallel experiments from the viewpoint of metal content in the wastes. The determination of metals in the PVC-containing wastes gave the average value of 26g/kg with less than 3% deviation from both experimental results. The average for four parallel experiments (12, 16, 11, and 33g/kg) was equal to 18g/kg. As can be seen from these results, one value was significantly higher than the average. However, considering that removal of solid pieces, that looked like metals, from the residue was a subjective process, and that experiment 10 showed the maximum value of 33g/kg for the amount of the metals removed from the solid residue, it was possible to assume that the removed pieces of solids could contain oxides that were not supposed to be removed from the residue. If this were the case, the amount of

metals in the waste for experiment 10 could go down to the content of the metals in the wastes for experiment 5, 6, and 9.

The values for metals content in cellulose, PU, and MX that were equal to 11, 8, and 8 g/kg together with the average value of 26 g/kg for PVC were used to estimate the metal content in the mixtures 4, 5, 6, 9, and 10. The calculated value for metals content in experiment 4 was equal to 8 g/kg (experimental value was 8 g/kg). The calculated value for the metals content in experiments 5, 6, 9, and 10 was equal to 13 g/kg (the average experimental value was 18 g/kg). With the account of unavoidably wide scatter of the metals content in the residue, both calculations support a correctness of the determinations of metals in the JET housekeeping wastes.

The ash residue in all the tests showed mildly alkaline reaction. Note that this alkalinity increased after calcining to 900°C (see the data for experiment 4). In part this can be assigned to loss of chlorine from iron chloride; apparently, the solid residue contained also metal carbonates, which decomposed during calcining.

Noteworthy, the residual ash content of the cellulose sample determined during preliminary experiments was 2.7%. Therefore, either the cellulose stock was not uniform in its ash content or a part of the ash collected was attributable to the oxidation of the fresh surface of the solid inert material.

The above data show that gasification of JET soft housekeeping material secures a dramatic (at least by a factor of 18) reduction in the waste mass and even stronger reduction in the volume of the residue.

3.1.2. Analysis of Liquid Samples Collected in Condenser and Absorber

3.1.2.1. Spent Acetone Solution and Acetic Acid Solutions for Washing Absorber between Experiments

There was a possibility that some chemical compounds could be deposited in the absorber. Therefore, it was decided that between all experiments the absorber would be washed out twice with 1 L of acetone to clean the system for the next experiment. Acetone as a washout liquid was selected because it was assumed that chemical compounds solvable in aqueous solutions already were washed out. However, despite all these precautions, an absorber packing clog had happened during experiment 7, which added an additional step into the cleaning procedure - washing the absorber with acetic acid that formed the spent acetic acid solutions, which also could contain the chloroorganics under check.

The sequence of the experiments corresponds to the one specified in Table VII.

Analyses performed showed that concentrations of total Cl in the acetone washouts were at the same level for both washouts. Though all acetone washouts had concentrations higher than pure acetone, Cl-organics contents of them were comparable with the acetone washout of the absorber before the first experiment. The concentrations of chloroorganics in the acetic acid washouts were at the same level as in acetic acid blank. Though it was known that the absorber was clogged by solids from first six experiments, and the clogging disrupted experiment 7; but it was possible for

practical purposes to conclude that Cl-containing organic compounds as waste combustion products were absent among solid particles clogged absorber packing or they were not soluble in acetone. It was known that deposits formed during pyrolysis, especially fresh deposits, were soluble in acetone; therefore, the fact that the washing of the absorber did not allow the deposits to be dissolved in acetone, and acetic acid dissolved the clogging and at the same time showed the absence of Cl-organic compounds in the acetic acid washouts led to conclusion that the clogging was not done by low soluble Cl-organic compounds. It might be fair to state that the clogging was done by metals hydroxides or carbonates precipitated in the sodium carbonate solution.

3.1.2.2. Condensate and Entrained Solid Particles

Table IX summarizes the quantities and properties of the condensate collected during Experiments 1 – 11. It also shows the anticipated water content in the exhaust gas. This content was estimated via the quantity of propane consumed, which gave water as a combustion product during an experiment, and the data on element composition of particular waste samples determined during preliminary experiments.

The solutions collected from the condenser were filtrated through a paper filter preliminary weighted. Solid particles left on filter surface were dried together with the filter at 105°C until constant mass, cooled down and weighted again. Masses of the solid particles were used to estimate the percentage of solid particles formed from a waste during combustion. These masses were also used to estimate a mass reduction of the waste during combustion (See Table X). Note that this procedure provided a sum of solid particles entrained by the gas flow from the reactor and soot formation due to imperfect arrangement of combustion within the afterburner.

Table IX also showed the data for pH of the solutions collected from the condenser and concentration of chloride in it. Chloride concentrations were determined by titrating with mercury (II) nitrate.

The solutions were formed by water vapor released in combustion of the combustible gas formed of waste and propane and condensed in the condenser absorbing “acid” gases soluble in water. These data allowed determining a total concentration of “acid” gases formed during combustion. A volume and pH of condensate solution allowed estimating the quantity of hydrogen cation for absorbed “acid” gases. The “acid” gases here could be hydrogen chloride and fluoride, NO_x and SO_x, and carbon dioxide. Considering that carbon dioxide formed an exceedingly weak acid, the pH of the condensate was probably controlled by absorption of “acid” gases that formed strong acids.

Table IX shows that the chloride anion concentrations in the condensate formed for all combusted wastes were higher than the ones for hydrogen cation. For waste containing PVC the data differed significantly (by 20-30 times). Considering that PVC combustion released hydrogen chloride, we conclude that hydrogen chloride, most probably, partially reacted with metals/and or metal oxides and yielded water-soluble metal chlorides. The metals and metal oxides could be impurities of the waste forming flyash particles and/or corrosion products of the equipment materials. This inference

was supported by the condensate solutions being light green, which may be due to chromium(3+) salts from stainless steel condenser tubes.

Table IX also shows that condensates were acidic in all the waste combustion experiments except cellulose. This fact confirmed that “acid” gases were released during combustion of all the studied wastes except cellulose. This proves that even the housekeeping wastes such as PU that were not supposed to form “acid” gases during combustion actually released them. This supports the conclusion that the JET wastes could not be quantitatively characterized and had to be considered as wastes with an uncertain composition.

The total formation of water stemming from oxidation of waste charge and oxidation of propane additionally fed to the afterburner can be estimated. A comparison of the estimated water formed with the volume of the condensate collected provided an evaluation for the efficiency of the condenser.

Table X shows the data for solid particles formed as waste combustion products and entrained by gas flow to the condenser and/or corrosion of aftercombustion chamber and/or condenser. These solid particles were insoluble in the acidic media. An estimate of their size distribution was also made.

Table XI summarizes the quantities and properties of the sodium carbonate solutions from the absorber collected during Experiments 1 – 11. For some experiments, distilled water was supplied upon completion of combustion to wash the absorber of the carbonate solution. This water is also included in the spent solution collected. The concentration of chloride anion is the average of two duplicate titrations with mercury nitrate.

An estimate of “acid” gases absorbed by sodium carbonate solution was also made, and the results are shown in Table XI. A decrease in the pH for the absorbate can be explained not only by absorption of strongly acidic gases formed during combustion but also by carbon dioxide absorption that could react with sodium carbonate forming hydrocarbonate. The solid particles of metal oxides, hydroxides, and chlorides formed during combustion or as corrosion products of the equipment could react with sodium carbonate solution forming hydroxides or carbonates. The metal hydroxides and carbonates could be deposited in the absorber, dissolved, or suspended in the absorbate.

It is interesting to note that for the former four experiments, unlike the condensate solutions, concentrations of hydrogen cation in absorbate were higher than the ones for chlorides. This probably says that the decrease in the pH is not mainly related to hydrogen chloride absorption and neutralization but to carbon dioxide.

3.1.2.4. Inorganic Anions, Halogen, Sulfur, and Nitrogen-Containing Organic Compounds in Mixture of Condensate and Absorbate Solutions

Tables IX-X showed that the ratios between concentrations of hydrogen cations and chlorides in condensate and absorbate allowed considering different chemical reactions that could lead to different complicated chemical compositions for the condensate and absorbate. The analytical work for determination of these compositions that allowed making some conclusions about waste combustion

products obtained in the experiments would be rather expensive and time-consuming. Taking into consideration that the goal of this research stage was to compare two different technologies, the condensate and absorbate solutions were combined into one solution, in which inorganic anions and organic compounds containing nitrogen, sulfur and halogens were determined according to procedures described in Section II.4.2.

Table XII shows the chloride, fluoride, nitrate, nitrite, and sulfate anions in the mixed solution determined by ion chromatography. All the concentrations are higher than the respective blanks by at least one order of magnitude. The presence of these inorganic anions in the mixed solutions witnessed that they were waste combustion products. It is interesting to note that contents of these anions formed during combustion of cellulose, PU, and Mixed Waste were on the same level of magnitude except fluorides, which had lower concentrations. N-, S-, and Hal-containing organic compounds were also found in the mixed solutions confirming that the presence of respective elements in the waste will lead to formation of organic compounds with these inorganic elements. Usually, presence of Cl-containing organic compounds can be an indicator of possible PCDD/PCDF formation.

Table XII shows that the concentrations of chloroorganic compounds were not directly dependent on chlorine content in a waste. An increase in chlorine content in the wastes was not accompanied by an increased formation of Cl- organic compounds.

3.1.2.5. Polychlorinated Dibenzodioxins/Furans as Waste Combustion Products

Table XIII shows the results of determination of polychlorinated dibenzodioxins/furans (PCDD/PCDF) in the mixture of condensate and absorbate and in the gas phase after the absorber. Expectedly, combustion of wastes containing PVC gave much higher PCDD/PCDF concentrations in gas phase and in absorbate solution than the wastes without PVC.

3.1.2.6 Determination of PVC Content in PVC-Containing Wastes

The analysis of residual ashes and liquids obtained during passing waste combustion products through the condenser and absorber provided the data necessary to estimate the concentration of chlorine in the Cl-containing wastes.

Chlorine was the element of interest through this research as, in effect, the chlorine (and chlorinated organics related to it) makes the only environmental concern (but for tritium itself) in processing the JET soft housekeeping waste, since concentrations of sulfur and fluorine in the waste stock proved insignificant. The concentration of chlorine was determined in the condensate, the absorbate, and in the residual ashes for all the experiments by using titration with mercury (II) nitrate. Chlorine was found in all the wastes, even where this element was not supposed to be a waste component. Table XIV shows the results of determination of chlorine in all subjects for the analytical procedures.

Table XIV shows that the concentration of chlorine in the PVC-containing waste is in the 26.6-32.4 % range. The average concentration of chlorine in PVC obtained in these experiments was

30%. This data provides an independent confirmation for the conclusion that was made during preliminary experiments (see Table IV). This is very important result because it allows making the conclusion that the system for collection of combustion products worked very well, especially for hydrogen chloride and other Cl-containing compounds. Considering that concentration of chlorine in pure PVC is 56.8%, it is possible to conclude that average PVC concentration in PVC group waste materials was 53%. Table XII. Analysis of Combined Liquid Sample for Countercurrent Gasification

3.2. PLASMA ARC CENTRIFUGE

3.2.1. Mass Spectrometry Determination of Gas Phase Composition

Table XV demonstrates the results for mass spectrometry determination of the composition of gas phases leaving the vacuum chamber of the PAC. Considering that mass spectrometry analysis usually is not used for water vapor concentration determination, samples were taken after first stage of condenser (9) where temperature was in a 100-150°C range for all final tests. During sampling the gas in an ampoule was cooled down to room temperature (~20°C) and water vapor concentrations also decreased to 2.33%.

The results specified in Table XV show that combustion of all studied materials was going without formation of carbon monoxide and nitrogen oxides (detection limits were ~0.05%vol). However, experiments 1, 2, and 5 showed hydrogen present in the sampled gaseous products. This indicates that 100% combustion for the housekeeping materials was not achieved.

Analysis of the temperature patterns for PAC combustion of the studied materials showed that average temperature in the chamber measured at the upper edge plane of the crucible and half way between the crucible and the chamber wall did not exceed ~650°C during process time for the experiments 1, 2, and 5. It is known that under such conditions hydrogen is more probable combustion product than carbon monoxide because at this temperature carbon monoxide is oxidized faster than hydrogen. At temperature higher than ~650°C, hydrogen is oxidized easier than carbon monoxide. Oxygen amount delivered to the crucible in experiments 1, 2, and 5 was more than theoretically required and still did not completely oxidize hydrogen; therefore, this was, probably, related to gas dynamic conditions in the crucible. The air coming into the crucible at room temperature has to be heated with the heat released by plasma arc. Considering that walls of the chamber are cooled with water, it is possible to conclude that hydrogen formed during combustion does not react with oxygen from air near the walls of the chamber due to low temperature, and hydrogen partially breaks through the chamber. This process can be improved by increasing the flow rate of air. An increase in the flow rate will improve oxygen balance in the hot reactive core within the crucible allowing more oxygen to react with hydrogen in the middle part of the crucible. Thus, it is possible to conclude that the experiments demonstrated that the PAC system is capable of treating the wastes with a good result meaning an absence of unreacted species as carbon monoxide or hydrogen in the PAC exhaust.

III.2.2. Residual Ash in Plasma Arc Centrifuge Combustion

It is necessary to note that residual ash was not discovered in the crucible of PAC after all the combustion experiments. This could mean that 100% of the wastes were transformed into a gas phase, or some unburned wastes and/or solid combustion products formed during combustion were entrained with the gas phase into the gas purification system. The experiments with metals definitely indicated that solid oxides formed during combustions were entrained by the gas flow. Masses of solid particles formed during combustion, entrained by gas phase and removed from the gas phase during passage through the condenser, bubbler, and filter were determined and are discussed later.

3.2.3. Analysis of Liquid Samples Collected in Bubbler and Filter

3.2.3.1. Spent Acetone Solution for Washing Filter between Experiments

There was a possibility that some chemical compounds could be deposited in the bubbler or filter. Therefore, it was decided that between all experiments the filter would be washed out with 1L of acetone to clean the system for the next experiment. Acetone as a washout liquid was selected because it was assumed that chemical compounds solvable in aqueous solutions were already washed out. The sequence of the experiments corresponds to the one specified in Table XV.

Analyses showed that concentrations of total Cl in the acetone washouts are at the same level. However, taking into consideration, that the relative standard deviation for this method of analysis was no more than 8%, it is possible to conclude that the concentrations for most of the experiments are statistically significant. After subtracting the total Cl concentration of Cl-containing organic compounds that were in acetone as impurities from Cl concentration of washouts, it was possible to conclude that a transfer of Cl-containing organic compounds from experiment to experiment was insignificant. Considering that total volume of acetone was 1L, quantity of total transfer from the bubbler to the filter was on a level of milligrams. = However, it is very important to note that even these small concentrations in acetone allow concluding that the JET housekeeping wastes contain components that were not shown in the JET waste Technical Specification.

3.2.3.2 Solid Particles as Waste Combustion Products

A combined solution collected from the condenser, the bubbler, and the filter was filtrated through a paper filter preliminary weighted. Solid particles left on the paper filter surface were dried together with the filter at 105°C until constant mass, cooled down, and weighted again. Masses of the solid particles were used to estimate formation of solid particles in combustion of a waste. These masses were also used to estimate the mass reduction factors (See Table XVI). As can be seen from Table XVI, the mass reduction was more than 97%, which is significant. A volume reduction was even greater.

Table XVI also shows the data for pH of the combined solution collected from the condenser, the bubbler, and the filter (the filter worked as a demister preventing entrainment of liquid to the vacuum pump). These data allowed determining a total concentration of “acid” gases formed during

combustion. A volume of an initial sodium carbonate solution used as the bubbler charge and a difference in pOH of the initial sodium carbonate solution and a solution after combustion allowed estimating a quantity of hydrogen ion for absorbed “acid” gases for the worst-case scenario, namely, when the change in pOH was related to hydrogen ion only without taking into consideration one more way of hydroxyl ion neutralization – reaction with carbon dioxide. These two reactions could be competitive in neutralization of hydroxyl ion. Knowing a quantity of a combusted waste allowed characterizing the wastes regarding these “acid gases” formation. As can be seen from Table XVI “acid” gases in experiments 1-8, in a quantity from 0.11 up to 0.18 g-equivalent of hydrogen cation, were released during combustion of 1 kg of the studied materials.

These data are very important for future research because “acid” gases could also be a tritium carrier. They also could be used to estimate a percentage of an individual waste specified in the JET wastes Technical Specification that might be in a composition of the certain wastes. For example, 1kg of a waste called PVC was supposed to release 16 g-equivalent of hydrogen cation during combustion if the waste were 100% PVC. However, as can be seen from Table XVI, the average amount of “acid” gases released in two combustion experiments (6 and 7) with a waste called PVC and collected in the sampling system was 0.13g-equivalent (0.11 and 0.15) of hydrogen cation. Calculation of PVC content in PVC-containing waste based on this value gives 0.81% PVC. This estimate contradicts the preliminary measurements of the element composition of PVC samples and measurements made during CG tests.

Considering that PVC combustion releases hydrogen chloride, it is possible to conclude that either hydrogen chloride broke through the bubbler, or partially reacted with metals/and or metal oxides and yielded water-soluble metal chlorides.

To check the assumption that hydrogen chloride broke through the bubbler, the bubbler volume was increased twofold from 5 to 10 liter for experiments 9 and 10. This resulted in an increase in concentration of hydrogen cation neutralized in the bubbler from 0.13 to 0.25g-equivalent/kg. Calculation of PVC content in PVC-containing materials based on this value gives 1.56% PVC. However, even this relatively significant increase could not explain where main amount of hydrogen chloride disappeared.

Table XVI shows that sodium carbonate solutions were partially neutralized in all these experiments. This fact confirmed that “acid” gases were released during combustion of all the studied wastes. This proves that even the housekeeping wastes, such as cellulose or PU, which were not supposed to form “acid” gases during combustion, released them. This further supports the conclusion that the JET wastes could not be quantitatively characterized and have to be considered as wastes with unknown compositions.

Table XVII also presents the data for size distribution of solid particles entrained by gas flow from the PAC chamber, and then removed from the gas phase by vapors condensation in the condenser and trapped by sodium carbonate solution in the bubbler. The solid particles isolated from the liquid by filtration on a paper filter were investigated by using an optical microscope.

The detection limit for optical microscope was 5mm. These measurements allowed determining a number of solid particles of a certain size, and then a size distribution based on full number of the solid particles. However, to estimate a size of equipment necessary to remove the solid particles in the future purification system, a mass percentage was calculated for the same fractions. To do so, the following assumptions were made:

- Solid particles were considered spherical;
- Density was assumed to be constant for all sizes of the of solid particles;
- Average diameter was applied to calculate mass percentage for a fraction. For example, for a fraction between 5 and 25 μm , an average diameter was 15 μm . For particles with size more than 500 μm , a cut-off value 600 μm was used.

3.2.3.3. *Inorganic Anions, Halogen, Sulfur and Nitrogen-Containing Organic Compounds as Waste Combustion Products*

A presence of chloroorganic compounds in acetone washouts was clear evidence that the bubbler solution should contain the same organic compounds. It was also known that at least wastes containing PVC would produce hydrogen chloride during combustion. As was discussed above, all the housekeeping wastes showed a release of “acid” gases during the waste combustion. “Acid” gases were absorbed by sodium carbonate solution forming respective inorganic salts. Table XVIII shows the measured concentrations of nitrogen-, sulfur- and halogen-containing organic compounds and inorganic anions.

As can be seen from Table XVIII, sulfur-containing organic compounds were not found at the detection level of 10^{-6} %mass used for this analysis but fluorine- and chlorine-containing organic compounds were found in all the sodium carbonate solutions. This is a very important finding because it again confirms that the JET wastes Technical Specification did not envision these elements (F and Cl) in compositions of all the wastes.

Comparing the content of F or Cl in the inorganic and organic forms showed that PU and Cellulose had higher content of organic Cl than inorganic one. With an increase in concentration of PVC in the mixtures of the wastes the concentration of inorganic Cl grew, whereas an increase in Cl content in the wastes did not significantly increase the organic Cl concentrations in the absorption solutions. For example, concentration of Cl- organic compounds formed during combustion of PU (1.8×10^{-3} %) and absorbed in the bubbler was on the same level with the concentration of Cl-containing organic compound for PVC (1.9 and 1.5×10^{-3} %) despite total chlorine content in PVC calculated based on the data for the concentrations of inorganic and organic compounds (See Table XVIII) was significantly higher (6-7% mass versus 0.04%mass). We do not have sufficient information at this stage of the research to explain how content of halogen in the waste affects the concentrations of halogen-containing organics formed during combustion provided a minimum of Cl content required for the reaction exists in the waste or this is due to the fact that the sodium carbonate solution is not good for the halogen-containing organic compounds absorption. However, these experiments allowed

characterizing the JET housekeeping wastes by establishing the additional elements of the waste compositions: fluorine in the range of 10^{-4} – 10^{-3} %mass; chlorine – 0.04-7.40%mass and sulfur – 0.02-0.042%mass.

A theoretical percentage of chlorine in PVC composition is 56.8%. Two experiments with all-PVC materials processed (See experiments 6 and 7) showed that, judging by the quantity of chlorine caught in the bubbler, the average concentration of chlorine in the PVC waste was 6.65%. This value is significantly higher than the one calculated based on the hydrogen cation data (maximum concentration of 1.56% was based on the data for experiments 9 and 10). Considering two values, it is possible to conclude that, most probably, hydrochloric acid partially reacted with metals/and or metal oxides and yielded water-soluble metal chlorides. The metals and metal oxides could be impurities of the waste forming flyash particles and/or corrosion products of the equipment materials. This inference is supported by the collected solutions having green shade, which may be due to chromium 3+ salts from stainless steel condenser tubes.

The results of element analysis of the various PVC materials supplied by UKAEA (Table III) showed that Cl contents in the materials were in a range of 20-36% mass. Comparing the results of element analysis with the ones obtained through PVC plasma arc centrifuge combustion products absorbed by the sodium carbonate we can name three possible reasons why chlorine in the element analysis was determined in the concentrations greater than the ones determined and shown in Table XVIII:

- Chlorine was in hydrogen chloride form but was not fully absorbed under such conditions;
- The PVC waste had many other unidentified impurities that were distributed uneven through the packages of the materials supplied by UKAEA, and the PVC materials used for the PAC experiments did not have the PVC concentrations in the materials at the level determined in element analysis, or;
- Molecular chlorine and hydrogen chloride were formed and molecular chlorine was not absorbed by sodium carbonate solution. If molecular chlorine were absorbed by the solution, it would react with formation of hypochlorite anions. If this were the case, hypochlorite anions would be detected and quantitatively measured with the methodology that was used to determine the inorganic anions. However, the results of the analysis showed no peaks attributed to hypochlorite anions. This indicated that if molecular chlorine was a combustion product of the JET soft housekeeping waste it did not have enough residence time in the solution to form hypochlorite anions and could break through the solution.

It is also possible that all three reasons are valid.

3.2.3.4. Polychlorinated Dibenzodioxin/Furan as Waste Combustion Products

Table XIX shows the results of determination polychlorinated dibenzodioxin/furan (PCDD/PCDF) in the liquid collected from the bubbler and filter and in the gas phase collected after the filter.

The analytical procedures used for an analysis of the spent bubbler's charge and gas phase allowed estimating total concentrations of the PCDD/PCDF formed during the wastes combustion following the cooling of combustion products in the chamber and condensers. The PCDD/PCDF formed are usually transported as sorbed on particulates surfaces and as vapors mixed with the gas phase. The particulates entrained with the gas phase were supposed to be separated in the bubbler from the gas. However, as can be seen from Table XVII a significant number of the solid particles (from 24% to 52%) have a diameter between 5 and 25 μm . Considering 5 μm detection limit, it is impossible to detect if the particles could have a smaller diameter and to determine a distribution inside this fraction. It is also known that even packed wet scrubbers, which are more efficient than bubblers, are efficient for removal of 5- μm or larger particulates [11]. Therefore, it was possible that a substantial fraction of the particulates broke through the bubbler. It is also unknown what percentage of these particles could break through the packed filter used as a demister. However, based on the visual observation of a filter used in a gas-sampling device, some of the particles broke through. It is interesting to note that all the wastes used for the combustion formed PCDD/PCDF. As can be seen from Table XIX, combustion of wastes containing PVC gave much higher PCDD/PCDF concentrations in gas phase and in the bubbler solution than the wastes without PVC.

4. COMPARISON OF PLASMA ARC CENTRIFUGE AND COUNTERCURRENT GASIFICATION METHODS

The goal of the research was to obtain comparative characteristics for Plasma Arc Centrifuge (PAC) and Countercurrent Gasification (CG) waste combustions. As could be seen from chapter III the experiments conducted allowed obtaining many similar characteristics that provide a basis for comparison.

One of the requirements for these experiments was to develop a system capable to treat 0.5-1kg/hour of the housekeeping waste. Both the PAC and CG systems achieved this goal.

One more requirement specified in the Technical Specification to the contract was to achieve reduction of volume of the waste by a factor of ten or greater. Both approaches gave the results significantly higher than volume reduction factor of ten.

The experiments for PAC and CG methods were designed the way to collect and analyze as many samples as possible within the contract budget to investigate the waste combustion products. Thus, the sampling systems used in the experiments were unavoidably also tested as prototype water recovery / gas cleansing systems.

Most important waste from a view of environmental protection was PVC because it was known that the combustion products of the PVC could produce very toxic compounds including PCDD/PCDF. However, considering possible fluctuations and uncertainties of the waste compositions, much attention was paid to determination of N-, S-, and Hal-containing organic compounds among all the housekeeping waste combustion products. Many of these toxic compounds were removed from the waste combustion products in gas purification systems. To obtain more detailed information about

forms, in which these elements could be present in the wastes, some inorganic anions were determined in the liquid products produced during work of the gas purification systems. Table XX presents the results of determination of these toxic organic compounds in the waste studied for both methods.

As can be seen from Table XX, the CG method formed smaller amount of Cl-, F-, and N-containing organic compounds than the PAC method for almost all the experiments. The average concentrations for chloroorganic compounds for the PAC were higher than the one for the CG method 5 times and for N-organic containing compounds, 4.4 times.

Table XXI shows the results of determination of the inorganic anions formed for both methods.

As can be seen from Table XXI, amount of chlorides trapped in the sampling system in all the experiments where chlorine element was present in the initial composition of the waste for the PAC method was significantly smaller than for the CG method. Several possible explanations for these results have already been discussed. One of them was a production of molecular chlorine that was not determined during these experiments. Indeed, one might expect a higher yield of the molecular chlorine in the PAC system distinguished by much higher temperatures. The production of molecular chlorine in a higher quantity could also be an explanation why Cl-containing organic compounds formed in the PAC experiments had the average concentrations 5 times higher than the ones for the CG method (see Table XX).

The wastes that were supposed to contain nitrogen were polyurethane and some PVC-containing wastes. However, as can be seen from Table XXI, nitrates and nitrites were formed in all the experiments for PAC and CG methods. The nitrates formation can be explained by the presence of nitrogen in air used and formation of nitrogen dioxide during combustion followed by its absorption with water for both methods but an origin of nitrites is unclear. Nitrogen oxide usually does not solve in aqueous solutions at any significant concentration. One possible explanation of nitrites presence in the solution could be nitrogen dioxide reaction with water that forms nitric acid and then disproportioning of nitric acid with formation of nitrites. The nitrates and nitrites concentrations were significantly higher for the PAC method when compared to the CG, especially for nitrites. Supposedly, this indicates that a much higher yield of nitrogen oxides was typical of PAC processing.

For the wastes that were not supposed to contain fluorine and sulfur in their composition, fluoride concentrations in the sodium carbonate solutions also were 3.3 times greater than for the CG. Only sulfate concentrations in the sodium carbonate solutions were more or less similar for both methods: 0.45g/kg waste for PAC and 0.51g/kg for CG.

It is also interesting to compare the results of determinations of hydrogen cation and chlorides. If during waste combustion hydrogen chloride is the only acidic product released, then collected amount of hydrogen cation in equivalents have to be equal to number of chlorides equivalents. Table XXII shows the results of hydrogen cation and chlorides determinations extracted from combustion products in PAC and CG experiments.

As can be seen from Table XXII, chlorides concentrations extracted from combustion products were significantly different: almost 4.7 times greater for CG versus PAC. This could be related to

the difference in efficiency of the HCl- recovery systems employed and the difference in the chemical form of the chlorine in the gas exhaust. In both CG and PAC experiments for PVC-containing wastes ratios between hydrogen cation and chloride concentrations were significantly less than 1 indicating that hydrogen cation was spent as a reactant, for example, with metals/metals oxides contained in compositions of the wastes and with materials of the equipment. For the PVC containing wastes, hydrogen chloride was supposed to be a product of combustion. The analysis of all-PVC type waste for CG experiments (See chapter 3.7.4.4) showed that approximately 30% of chlorine (~8.5g-equiv/kg) in the form of chlorides instead of theoretically possible of 56.8% was found. This means that the same amount of hydrogen cation (~8.5g-equiv/kg) had to be found in the experiments. However, average hydrogen/chloride ratio for two CG experiments with 100% PVC is 0.035 that corresponds to 0.3 g-equivalent of hydrogen cation per kg waste. The same situation was for PAC experiments with 100% PVC: average hydrogen/chloride ration is 0.07. The reasonable explanation for the case can be that hydrogen cation was reacted with metals/metals oxides with formation of water and chloride salts.

Table XXIII shows comparison of the data for solid particles formed during the soft housekeeping materials combustion and PCDD/PCDF extracted from the combustion products. The table shows that the amount of solid particles entrained from the combustion devices by the gas flows and recovered in a condenser/absorber system was significantly greater in all experiments for PAC data when compared to CG. As can also be seen from the table, CG data for former four experiments, in which the wastes did not have “official” content (based on UKAEA specification) of chlorine, indicated PCDD/PCDF formation 2-11 times greater than for respective PAC experiments. The experiments with higher chlorine content in the waste shows that CG data show lower total PCDD/PCDF concentrations for four cases and greater concentrations for two cases when compared to PAC. It is also interesting to note that PAC experiments in 7 cases from 10 indicated that PCDD/PCDF was concentrated in gas phase but CG experiments in 7 cases from 10 showed diametrically opposed picture. Usually, PCDD/PCDF is associated with solid particles that could sorb PCDD/PCDF on their surfaces. A quantitative data for the concentrations of the solid particles, which broke through the condenser/absorber system, were not collected in these experiments. Therefore, it is difficult to make any certain conclusion about the nature of PCDD/PCDF formation. However, it is possible to conclude that it is necessary to pay attention in the future experiments to a possibility determining PCDD/PCDF concentrations in liquids and gas separated from the particles.

Note that total recovery of entrained particles in PAC experiments was poor. As no ash was accumulated in the crucible, the content of ash in the waste processed must coincide with the total amount of entrained particulates.

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Material	Average Tritium Concentration (MBq/g)			Fraction of Inventory (%) ^{d)}	
	Combustion	Leaching and combustion	RLG	Water- soluble	Water non-soluble
Cellulose	25.9	3373	1155	99.97	0.03
PVC	59.7	360	373	89.4	10.6
PE	114	103	313	68	32
PP ^{b)}	18	24	146	45	55
Rubber ^{c)}	70.8	455	417	97.7	2.3
PU	23.5	579	223	99.6	0.4

a) PVC is polyvinylchloride; PE, polyethylene; PU, polyurethane

b) Polypropylene (PP) is a plastic of PE group.

c) Rubber is of Nitrile group

d) Was estimated from results of leaching followed by combustion

Table I: Tritium content in polymeric materials ^{a)}

Sample	Tritium concentration on surface (MBq/g)		
	Duration of exposure to tritium		
	1 hour	7 hours	100 hours
PVC group: 1	350	990	5770
2	110	900	3690
3	120	400	1390
4	580	600	13770
PE group: 1	550	730	790
2	570	1460	--
3	1070	1640	--
4	650	790	--
5	70	90	--
Rubber	680	1900	15850

Table II: Tritium concentration in polymeric materials

Sample	C	H	Cl	N	O [#]	Ash
PVC-1	46.1	6.2	34.1	5.2*		8.3
PVC-2	51.2	6.0	36.3	3.1*		3.5
PVC-3	56.2	7.2	29.1	0.0	7.5	0.0
PVC-4	51.5	6.8	33.2	3.7*		4.9
PVC-5	51.9	6.6	20.3	0.5	7.6	13.2
PVC-6	51.9	6.3	35.0	5.1*		1.7
PU-1	64.0	7.2	-	4.7	24.1	0.0
PU-2	62.9	7.2	-	4.3	23.5	2.2
Rubber	75.7	9.5	-	5.4*		9.4

[#]As residue

*N+O

Table III: Element Composition of Polymeric Samples, mass%

No	Content of material, mass %				
	PVC ^{a)}	PU ^{a)}	MX ^{a)}	Cellulose	Other materials
1	0	0	0	100	None
2	0	100	0	0	None
3	0	0	100	0	None
4	0	30	60	10	None
5	30	30	30	10	None
6	30	30	30	10	Metals
7	100	0	0	0	None
8	100	0	0	0	Metals
9	30	30	30	10	None
10	30	30	30	10	Metals

a) PVC is polyvinylchloride; PU, polyurethane; MX, Mixed Plastics, which included polyethylene, polyvinyl, polyester, polypropylene, and rubber.

Table IV: Composition of samples for the tests

	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
Detection Limit, g	1.1×10 ⁻¹¹	1.8×10 ⁻¹¹	3.1×10 ⁻¹¹	4.8×10 ⁻¹¹	2.3×10 ⁻¹¹

Table V: Ion Chromatography Detection Limits for F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻

Compound	Primary ion, M ₁	Secondary ion, M ₂	Theoretical value of peaks ratio, M ₁ /M ₂
PCDD/PCDF			
TetraCDD	320	322	0.77
TetraCDF	304	306	0.77
PentaCDD	356	358	1.32
PentaCDF	340	342	1.32
HexaCDD	390	392	1.24
HexaCDF	374	372	1.24
HeptaCDD	424	426	1.05
HeptaCDF	408	410	1.05
OctaCDD	458	460	0.89
OctaCDF	442	444	0.89
Internal standard-surrogates			
2-Fluoro-6,7,8,9-tetraCDD	338	340	0.77
¹³ C ₁₂ -2,3,7,8-tetraCDD	332	334	0.77
¹³ C ₁₂ -1,2,3,7,8-pentaCDD	386	370	1.32
¹³ C ₁₂ -1,2,3,6,7,8-hexaCDD	402	404	1.24
¹³ C ₁₂ -1,2,3,4,6,7,8-heptaCDD	436	438	1.05
¹³ C ₁₂ -octaCDD	470	472	0.89

Table VI: Characteristic ion masses (m/z) of target PCDD/PCDF and internal standard-surrogates

Test #	Waste Composition	Waste Charge Mass	Waste Charge volume	Total Combustion Time*	Consumption Time for Charge	Residual Ash Mass**	Mass Reduction Factor
		g	L	min	min	G	
1	100%Cellulose	1100	15.0	87	55	60.0	18.3
2	100%PU	1200	5.1	96	53	33.2	36.1
3	100%Mixed Plastics (MX)	1200	7.7	101	58	25.9	46.3
4	30%PU+60%MX+10%Cellulose	1200	8.0	99	58	32.3	37.2
5	30%PU+30%MX+30%PVC+10%Cellulose	1200	7.7	128	55	56.4	21.3
6	30%PU+30%MX+30%PVC+10%Cellulose+Me	1272	7.3	93	56	124.3	10.3
7	100%PVC	1200	4.7	78	52	62.4	19.2
8	100%PVC+Me	1272	5.1	102	46	137.8	9.2
9	30%PU+30%MX+30%PVC+10%Cellulose	1200	7.2	89	40	61.1	19.6
10	30%PU+30%MX+30%PVC+10% Cellulose + Me	1272	7.9	139	52	150.6	8.4
11	100%PVC	1200	5.1	103	63	69.41	17.3

*Total combustion time is the time from the afterburner ignition until it is turned off. This includes:

- The time of heating up aftercombustion chamber at the beginning of the experiments;
- The time of waste combustion in the reactor, and;
- The time when last releases from already burned ashes are completed.

**Including metals

Table VII: Experimental Conditions for Final CG Tests

	1	2	3	4	5	6	7	8	9	10	11
Waste Charge, g	1100	1200	1200	1200	1200	1272	1200	1272	1200	1272	1200
Residue Mass, g	82.6	78.9	31.5	41.0	56.4	124.3	102.5	137.8	61.1	150.6	69.4
Residue Volume, mL	400	400	160	160		400		400		400	
Residual Ash Mass, g	60	25.0**	25.7**	32.3*	56.4	46.7**	62.4	52.1**	61.1	51.6**	69.4
Density of Residual Ash, g/cm ³	0.18	0.24	0.18	0.27 0.19***	0.19	0.18	0.25	0.20	0.17	0.17	0.16
Metals in Solid Residue, g	-	8.2	0.2	-	-	77.6	-	85.7	-	99	-
pH of Leaching Solution	8.76	11.61	9.25	8.46 9.27***	8.30	8.20	10.25	8.29	9.78	9.67	7.19
[Cl ⁻] in the Leaching Solution of Solid Residue, g-equiv/L.	0.0015	0.00045	0.080	0.083 0.031***	0.164	0.092	0.040	0.102	0.090	0.100	0.092
Total Content of Cl in Solid Residue, g	0.064	0.011	1.47	2.41 0.71***	6.57	3.05	1.77	3.77	3.90	3.66	4.53
Element Analysis of Residual Ash											
Residual Ash Sample Mass, g	0.5117	0.4711	0.4702	0.4244	0.5711	0.5667		0.4758	0.4278	0.5841	0.5463
Insoluble Residue, g	0.2389	0.3444	0.1288	0.1120	0.1534	0.1123		0.0554	0.1028	0.1440	0.0578

Metals in Residual Ash, mg/kg	1	2	3	4	5	6	7	8	9	10	11
Si	239	107	177	112	8.2	12.4		14.7	12	17.6	17.1
Al	71330	8420	18000	20190	50390	5790		93390	41050	62490	60040
Mg	9390	6020	9620	10230	5000	3080		3300	3750	3820	1460
Ca	250120	91060	319330	252710	174020	100940		66120	117500	99640	52550
Fe	11340	13720	126360	75760	114440	64140		101370	112740	33030	354430
Mn	817	1730	1450	547	610	615		846	543	400	740
Ti	5850	17550	28660	23640	703	275		768	140	216	905
Na	29180	5750	2090	8175	6950	5985		2920	5810	6000	2650
Cu	111	87	1850	1490	875	172050		118220	13090	113850	5125
Ni	150	151	561	94	145	670		225	94	122	123
Co	9	22	44	31	12	10		19	10	6	33
Cr	194	327	500	187	244	135		328	144	190	108
Cd	0.78	1.06	0.85	1.18	60.15	63.35		200.0	94.8	104.5	271.8
Be	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		<1.0	<1.0	<1.0	<1.0
Metals in Waste, g/kg****	11	8	8	8	12	16		26	11	33	25
Anticipated Metals Content in Mixtures*****				8	13	13			13	13	
	1	2	3	4	5	6	7	8	9	10	11

* Calculated according to mass loss measured on aliquot;

**The residual ash mass was determined as a difference between the mass of the solid residue and mass of metals obtained after separation of metal from the solid residue (after calcining when the solid residue contained a substantial part of char);

*** After calcining at 900°C;

**** Masses of added metals in Experiments 6, 8, and 10 were not taken into consideration in the estimates;

*****Metals content in mixtures calculated using experimental data obtained for individual wastes. Average metals content in PVC used for calculation of metals content in mixtures (experiments 4, 5, 6, 9, and 10).

Table VIII: The characteristics of solid residue for Experiments 1 – 11

	Waste composition	Volume of Solution supplied to absorber	Sodium carbonate concentration	Volume of Solution Collected	pH of Solution measured by pH-meter	Concentration of Hydrogen Cation in Absorbate	Concentration of Cl ⁻ determined by titration	Total Cl in Solution
		L	g/L	L		g-equiv./L	g-equiv/L	g
1	100%Cellulose	7.3	5	7.175	9.12	0.0031	0.0003	0.08
2	100%PU	5.0	5	4.120	8.53	0.0031	0.0003	0.04
3	100%Mixed Plastics (MX)	4.8	5	4.160	8.67	0.0031	0.006	0.89
4	30%PU+60%MX+10%Cellulose	6.3	5	6.020	8.58	0.0031	0.0014	0.30
5	30%PU+30%MX+30%PVC+10%Cellulose	8.3	20	7.610	8.43	0.006	0.13	35.12
6	30%PU+30%MX+30%PVC+10%Cellulose+Me	12.0	20	11.400	8.01	0.006	0.051	20.64
7	100%PVC	5.0	50	5.680	8.27	0.010	0.20	40.33
8	100%PVC+Me	12.0	50	11.820	8.61	0.010	0.154	64.62
9	30%PU+30%MX+30%PVC+10%Cellulose	4.8+1.0***	20	6.720	8.10	0.006	0.040	9.54
10	30%PU+30%MX+30%PVC+10%100%PVC Cellulose + Me	7.4+3.0***	20	11.720	8.03	0.006	0.037	15.39
11	100%PVC	9.5+2.5***	50	11.320	8.19	0.010	0.166	66.71

***Distilled water for washing the absorber

Table XI: Sodium Carbonate Solutions from Absorber

Test Number	Waste Composition	Nitrogen-Containing Organic Compounds	Sulfur-Containing Organic Compounds	Halogen-Containing Organic Compounds		Inorganic Anions Concentration in Combined Liquid Sample* %mass				
		N, %mass	S, *10 ⁻⁶ %mass	F, *10 ⁻⁶ %mass	Cl, *10 ⁻⁴ %mass	F ⁻	Cl ⁻	NO ₂	NO ₃	SO ₄ ²⁻
	Sodium Carbonate	< 4.18*10 ⁻⁷		4.5	0.9	<2.4*10 ⁻⁶	<3.1*10 ⁻⁴	<5.1*10 ⁻⁶	<7.1*10 ⁻⁵	<3.0*10 ⁻⁶
1	Cellulose	< 4.18*10 ⁻⁷	<1	5.2	4.6	1.5*10 ⁻⁵	1.4*10 ⁻³	1.3*10 ⁻³	1.1*10 ⁻⁴	3.4*10 ⁻³
2	PU	5.20*10 ⁻⁶		4.9	3.9	1.6*10 ⁻⁵	0.9*10 ⁻³	2.5*10 ⁻³	2.2*10 ⁻⁴	1.2*10 ⁻³
3	Mixed Plastics (MX)	6.82*10 ⁻⁶	<1	5.0	5.1	1.6*10 ⁻⁵	0.065	0.9*10 ⁻³	2.2*10 ⁻⁴	7.8*10 ⁻³
4	30%PU+60%MX+10%Cellulose	6.17*10 ⁻⁶	<1	5.2	3.8	1.5*10 ⁻⁵	0.021	2.1*10 ⁻³	1.5*10 ⁻⁴	7.1*10 ⁻³
5	30%PU+30%MX+30%PVC+10%Cellulose	1.38*10 ⁻⁶	<1	5.5	4.9	1.6*10 ⁻⁵	0.58	1.1*10 ⁻³	2.2*10 ⁻⁴	7.0*10 ⁻³
6	30%PU+30%MX+30%PVC+10%Cellulose+Me	< 4.18*10 ⁻⁷	<1	4.9	4.1	0.9*10 ⁻⁵	0.65	<1.0*10 ⁻⁴	2.0*10 ⁻⁴	9.1*10 ⁻³
8	PVC+Me	2.27*10 ⁻⁵	<1	5.5	4.9	1.0*10 ⁻⁵	2.03	<1.0*10 ⁻⁴	2.4*10 ⁻⁴	4.2*10 ⁻³
9	30%PU+30%MX+30%PVC+10%Cellulose	6.24*10 ⁻⁵	<1	5.6	4.8	2.3*10 ⁻⁵	1.44	<1.0*10 ⁻⁴	1.9*10 ⁻⁴	7.0*10 ⁻³
10	30%PU+30%MX+30%PVC+10%Cellulose+Me	2.32*10 ⁻⁵	<1	5.1	4.4	2.7*10 ⁻⁵	0.72	<1.0*10 ⁻⁴	1.5*10 ⁻⁴	9.2*10 ⁻³
11	PVC	1.18*10 ⁻⁵	<1	5.5	5.0	1.2*10 ⁻⁵	3.42	<1.0*10 ⁻⁴	2.5*10 ⁻⁴	7.1*10 ⁻³

* Determined by ion chromatography

Table XII: Analysis of combined liquid sample for countercurrent gasification

	1	2	3	4	5	6	7	8	9	10	11
Total volume (L)	8.640	5.486	6.000	7.470	8.450	14.470	7.580	13.850	8.800	13.655	12.955
Condensate/ Adsorbate Mixture, TEQ, (pg/L)	278	331	1.28E+3	1.04E+3	3.45E+3	8.48E+4	-	3.59E+5	1.31E+5	1.27E+5	8.06E+4
Total volume (m ³)*	22.3	23.6	28.3	20.7	19.7	23.6	16.2	15.2	12.1	19.3	8.7
Gas Phase, TEQ, (pg/m ³)	63	719	209	308	2.37E+3	8.9E+4	1.56E+5	1.97E+5	1.67E+4	1.18E+4	1.15E+4

*Estimated as the sum of primary (gasification) and secondary (aftercombustion) air

Yield of PCDD/PCDFs was calculated as Toxic Equivalent (TEQ) using measured concentrations (C) and Toxic Equivalency Factor (TEF) for each individual PCDD/PCDF. $TEQ = \sum(C \cdot TEF)$ is a means of expressing the toxicity of a complex mixture of different PCDD/PCDF 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 [10].

Table XIII: PCDD/PCDF Concentrations (TEQ) in Condensate/Absorbate Mixture and Gas Phase after Absorber for tests I - II

Test Number	Condensate g	Absorbate g	Solid Residue g	Total g	Mass of PVC-Group Waste g	Cl/PVC %mass
1	0.4	0.08	0.064	0.54		
2	0.1	0.04	0.008	0.15		
3	5.7	0.89	1.47	8.1		
4	3.5	0.30	2.41	6.2		
5	66.8	35.12	6.57	108.5	360	30.1
6	87.2	20.64	3.05	110.8	360	30.8
7	277.2	40.33	1.77	319.3	1200	26.6
8	271.7	64.62	3.77	340.1	1200	28.3
9	103.4	9.54	3.90	116.8	360	32.4
10	87.2	15.39	3.66	106.3	360	29.5
11	289.6	66.71	4.53	360.6	1200	30.0

Table XIV: Chlorine Content in Subject of Analysis in Experiments

Test No.	Waste Composition	Mass,	Combustion	Sampling	Gas Phase Concentration, %vol. (by mass spectrometry)				
		g	time, min	time *, min	H ₂	N ₂	O ₂	Ar	CO ₂
1	Mixed Plastics (MX)	440	40	5	4.4	87.9	2.0	1.00	4.7
				20	2.5	88.7	2.1	1.0	5.7
2	Cellulose	300	30	5	0.3	83.7	11.3	1.0	3.7
				25	0.3	83.2	11.3	1.1	4.1
3	PU	500	55	7		83.8	12.9	1.1	2.3
				20		85.2	9.2	1.1	4.5
				40		84.2	9.9	1.1	4.7
4	30%PU+60%MX +10%Cellulose	500	60	5		89.6	1.6	1.1	7.7
				21		87.2	9.0	0.9	2.9.
				46		89.2	3.1	1.0	6.7
5	30%PU+30%MX +30%PVC+10% Cellulose	400	40	6	3.0	88.0	1.1	1.0	6.9
				25	3.0	88.0	1.3	1.1	6.6
6	PVC	500	60	7		83.1	14.1	1.1	1.6
				20		83.1	13.7	1.2	2.0
7	PVC+Me	400	40	7		86.2	8.0	1.0	4.8
				28		84.3	10.8	1.1	3.6
8	30%PU+30%MX +30%PVC+10% Cellulose+Me	500	60	7		83.1	12.9	1.1	2.9
				23		83.0	14.6	1.1	1.2
9	30%PU+30%MX +30%PVC+10% Cellulose	500	68	30		84.8	14.1		1.0
10	30%PU+30%MX +30%PVC+10% Cellulose+Me	500	52	10		83.6	13.7	0.95	1.7
				10		84.5	11.61	0.971	2.8
				35		85.4	0.7	.0	2.8

* After start of the test

Table XV: PAC Combustion Gas Phase Composition

Test No	Sample Composition	Mass	Volume of Liquid Collected in Bubbler and Filter	pH of Liquid	Solid Particles Concentration in Volume of Liquid	Concentration of Solid Particles Left after Waste Combustion per Waste	Acid Gases Formation per Waste g-eqv/kg	Waste Mass Reduction %mass
		g	L		mg/L	%mass		
	Sodium Carbonate			12.1				
1	Mixed Plastics (MX)	440	5.38	11.1	1.85	2.26	0.14	97.74
2	Cellulose	300	5.05	11.21	0.95	1.60	0.18	98.40
3	PU	500	4.95	10.75	0.95	0.94	0.12	98.40
4	30%PU+60%MX +10%Cellulose	500	4.93	10.8	1.35	1.33	0.12	98.67
5	30%PU+30%MX +30%PVC+ 10%Cellulose	400	5	10.35	1.8	2.25	0.15	97.75
6	PVC	500	4.55	9.7	3.2	2.84	0.11	97.16
7	PVC+Me	400	4.83	9.75	1.95	2.35	0.15	97.65
8	30%PU+30%MX +30%PVC+ 10%Cellulose+ Me	500	4.28	10.15	1.8	1.54	0.11	98.46
9	30%PU+30%MX +30%PVC+ 10%Cellulose	500	10	10.42	0.35	0.70	0.25	99.30
10	30%PU+30%MX +30%PVC+ 10%Cellulose+ Me	500	10	9.50	0.80	1.60	0.25	98.40

Table XVI: Solid Particles as Waste Combustion Products

Test No.	Waste Composition	Solid Particles Size Distribution													
		% from Number of Particles							%mass						
		<25µm	<50µm	<100µm	<150µm	<300µm	<500µm	>500µm	<25µm	<50µm	<100µm	<150µm	<300µm	<500µm	>500µm
1	Mixed Plastics (MX)	41	27	17	9	5	1		0.09	0.97	4.87	11.94	38.67	43.46	
2	Cellulose	46	25	16	11	2			0.30	2.51	12.86	40.93	43.40		
3	PU	43	28	16	10	3			0.23	2.38	10.87	31.46	55.05		
4	30%PU+60%MX+10%Cellulose	47	20	18	8	6	1		0.10	0.67	4.84	9.97	43.59	40.82	
5	30%PU+30%MX+30%PVC+10%Cellulose	37	15	7	12	15	11	3	0.01	0.06	0.21	1.67	12.19	50.24	35.62
6	PVC	24	24	30	15	7			0.07	1.03	10.29	23.81	64.81		
7	PVC+Me	47	36	11	5	1			0.57	6.82	16.66	35.06	40.89		
8	30%PU+30%MX+30%PVC+10%Cellulose+Me	52	35	6	4	2	1		0.18	1.86	2.55	7.88	22.98	64.55	
9	30%PU+30%MX+30%PVC+10%Cellulose	50	20	11	8	6	5		0.04	0.26	1.13	3.81	16.68	78.08	
10	30%PU+30%MX+30%PVC+10%Cellulose+Me	47	20	13	7	7	3	3	0.02	0.13	0.69	1.73	10.08	24.27	63.08

Table XVII: Solid Particles Size Distribution

Test	Waste Composition	Nitrogen-Containing Organic Compounds	Sulfur-Containing Organic Compounds	Halogen-Containing Organic Compounds		Inorganic Anions Concentration, %mass				
		N, %mass	S, *10 ⁻⁶ %mass	F, *10 ⁻⁶ %mass	Cl, *10 ⁻³ %mass	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
	Blank for tests 1-8 Sodium Carbonate	< 4.18×10 ⁻⁷		1.9	0.11	2.4*10 ⁻⁶	0.8*10 ⁻⁴	3.2*10 ⁻⁵	1.8*10 ⁻⁵	1.0*10 ⁻⁴
1	Mixed Plastics (MX)	6.80×10 ⁻⁶	<1	2.6	1.3	9.8*10 ⁻⁵	0.6*10 ⁻²	0.3*10 ⁻²	3.4*10 ⁻⁴	2.2*10 ⁻³
2	Cellulose	< 4.18×10 ⁻⁷	<1	2.9	1.4	9.2*10 ⁻⁵	0.1*10 ⁻²	0.4*10 ⁻²	3.6*10 ⁻⁴	2.6*10 ⁻³
3	PU	1.50×10 ⁻⁴		2.1	1.8	3.0*10 ⁻⁵	0.2*10 ⁻²	0.8*10 ⁻²	3.8*10 ⁻⁴	3.5*10 ⁻³
4	30%PU+60%MX+10%Cellulose	4.00×10 ⁻⁵	<1	3.4	1.1	3.0*10 ⁻⁵	0.3*10 ⁻²	1.1*10 ⁻²	4.2*10 ⁻⁴	2.0*10 ⁻³
5	30%PU+30%MX+30%PVC+10%Cellulose	4.81×10 ⁻⁵	<1	1.5	0.9	2.8*10 ⁻⁵	5.8*10 ⁻²	0.4*10 ⁻²	4.6*10 ⁻⁴	2.8*10 ⁻³
6	PVC	8.96×10 ⁻⁶	<1	2.5	1.9	7.6*10 ⁻⁵	6.5*10 ⁻¹	1.6*10 ⁻¹	4.9*10 ⁻⁴	2.9*10 ⁻³
7	PVC+Me	1.55×10 ⁻⁵	<1	3.0	1.5	9.8*10 ⁻⁵	6.1*10 ⁻¹	0.8*10 ⁻¹	3.4*10 ⁻⁴	3.2*10 ⁻³
8	30%PU+30%MX+30%PVC+10%Cellulose+Me	4.05×10 ⁻⁵	<1	2.9	0.8	4.4*10 ⁻⁵	6.8*10 ⁻²	4.3*10 ⁻²	5.6*10 ⁻⁴	2.5*10 ⁻³
	Blank for tests 9-10 Sodium Carbonate			3.2	0.15	1.2*10 ⁻⁵	6.7*10 ⁻⁵	2.1*10 ⁻⁵	1.8*10 ⁻⁵	1.9*10 ⁻⁵
9	30%PU+30%MX+30%PVC+10%Cellulose	4.13×10 ⁻⁵	<1	3.9	1.3	1.8*10 ⁻⁵	0.8*10 ⁻¹	2.3*10 ⁻²	1.1*10 ⁻⁴	1.0*10 ⁻³
10	30%PU+30%MX+30%PVC+10%Cellulose+Me	5.92×10 ⁻⁵	<1	3.8	1.1	2.2*10 ⁻⁵	2.5*10 ⁻¹	6.6*10 ⁻¹	0.8*10 ⁻⁴	1.1*10 ⁻³

Table XVIII: Analysis of Combined Liquid Sample Collected from Bubbler and Packed Filter for PAC Combustion

	1	2	3	4	5	6	7	8	9	10
Total Volume, L	5.38	5.05	4.95	4.93	5	4.55	4.83	4.28	10.0	10.0
Liquid from Bubblers and Packed Filter, TEQ, (pg/L)	1555	225.9	1330	3233	7695	3.97E+04	5299	5.11E+04	8.68E+04	6.96E+04
Total Volume, m ³	7.2	5.4	9.9	10.8	7.2	10.8	7.2	10.8	12.24	9.36
Gas Phase, TEQ, (pg/m ³)	6282	1553	960.2	3413	2891	1.85E+05	3.86E+04	6.33E+04	3.72E+04	1.45E+04

a) Yield of PCDD/PCDFs was calculated as Toxic Equivalent (TEQ) using measured concentrations (C) and Toxic Equivalency Factor (TEF) for each individual PCDD/PCDF. $TEQ = S(C \hat{\nu} TEF)$ is a means of expressing the toxicity of a complex mixture of different PCDD/PCDF 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 [10].

Table XIX. PCDD/PCDF (TEQ) Concentrations in Liquid Collected from Bubbler and Packed Filter and in Gas Phase after Packed Filter^{a)}

	Cl Organic, g/kg Waste		F Organic, g/kg Waste		N Organic, g/kg Waste		S Organic, g/kg Waste	
	PAC	CG	PAC	CG	PAC	CG	PAC	CG
100% Cellulose	0.22	0.03	1.68E-04	5.50E-05	<1.39E-06	<3.80E-07	<1.68E-04	<5.50E-05
100% PU	0.17	0.01	1.98E-05	1.83E-05	1.48E-02	2.19E-04	<1.98E-05	<1.83E-05
100% Mixed Plastics	0.15	0.02	8.56E-05	2.50E-05	7.80E-04	3.20E-04	<8.56E-05	<2.50E-05
30%PU+60%MX+10%Cellulose	0.10	0.02	1.48E-04	4.53E-05	3.90E-03	3.72E-04	<1.48E-04	<4.53E-05
30%PU+30%MX+30%PVC+10%Cellulose	0.10	0.03	<3.75E-06	7.04E-05	5.96E-03	6.77E-05	<1.10E-11	<7.04E-05
30%PU+30%MX+30%PVC+10%Cellulose+Me	0.06	0.04	8.56E-05	4.82E-05	3.43E-03	<3.29E-07	<8.56E-05	<4.82E-05
100%PVC+Me	0.17	0.05	1.33E-04	1.15E-04	1.82E-03	2.43E-03	<1.33E-04	<1.15E-04
30%PU+30%MX+30%PVC+10%Cellulose	0.23	0.03	1.40E-04	8.07E-05	8.18E-03	4.55E-03	<2.00E-04	<8.07E-05
30%PU+30%MX+30%PVC+10%Cellulose+Me	0.19	0.04	1.20E-04	6.83E-05	1.18E-02	2.45E-03	<2.00E-04	<6.83E-05
100%PVC	0.16	0.04	5.46E-05	1.08E-04	7.77E-04	1.23E-03	<5.46E-05	<1.08E-04

Table XX: Hal-, N-, and S-containing Compounds Extracted from Combustion Products in PAC and CG Experiments

	Cl, g/kg Waste		F, g/kg Waste		NO ₂ ⁻ , g/kg Waste		NO ₃ ⁻ , g/kg Waste		SO ₄ ²⁻ , g/kg Waste	
	PAC	CG	PAC	CG	PAC	CG	PAC	CG	PAC	CG
100% Cellulose	0.15	0.11	1.14E-02	1.06E-03	0.668	0.102	0.058	0.008	1.263	0.267
100% PU	0.19	0.04	5.94E-04	6.63E-04	0.789	0.114	0.036	0.010	0.337	0.055
100% Mixed Plastics	0.72	3.25	9.05E-03	7.25E-04	0.363	0.045	0.039	0.011	0.257	0.390
30%PU+60%MX+10%Cellulose	0.29	1.36	5.92E-04	8.74E-04	1.081	0.136	0.040	0.009	0.187	0.460
30%PU+30%MX+30%PVC+10%Cellulose	7.24	40.84	5.00E-04	1.02E-03	0.496	0.077	0.055	0.015	0.338	0.493
30%PU+30%MX+30%PVC+10%Cellulose+Me	2.91	78.38	1.71E-03	9.04E-04	3.678	0.011	0.046	0.023	0.205	1.097
100%PVC+Me	73.65	234.1	8.94E-03	9.81E-04	9.656	0.011	0.039	0.027	0.374	0.484
30%PU+30%MX+30%PVC+10%Cellulose	15.99	105.3	1.20E-03	1.58E-03	190.0	0.007	0.02	0.013	0.589	0.513
30%PU+30%MX+30%PVC+10%Cellulose+Me	49.99	82.3	2.00E-03	2.90E-03	132.0	0.011	0.01	0.016	0.649	1.047
100%PVC	59.14	368.9	4.73E-03	1.13E-03	14.557	0.010	0.043	0.026	0.255	0.766

Table XXI: Inorganic Anions Extracted from Combustion Products in PAC and CG Experiments and Determined by Ion Chromatography

	Cl ⁻ , g-equiv/kg Waste		H ⁺ , g-equiv/kg Waste		H ⁺ /Cl ⁻	
	PAC	CG	PAC	CG	PAC	CG
100% Cellulose	0.004	0.003	0.180	0.020	41.26	6.45
100% PU	0.005	0.001	0.120	0.011	22.41	9.89
100% Mixed Plastics	0.020	0.092	0.140	0.059	6.87	0.65
30%PU+60%MX+10%Cellulose	0.008	0.038	0.120	0.061	14.80	1.61
30%PU+30%MX+30%PVC+10%Cellulose	0.20	1.15	0.150	0.260	0.74	0.23
30%PU+30%MX+30%PVC+10%Cellulose+Me	0.16	2.21	0.110	0.186	0.67	0.08
100%PVC+Me	2.07	6.60	0.150	0.265	0.07	0.04
30%PU+30%MX+30%PVC+10%Cellulose	0.45	2.98	0.247	0.157	0.55	0.05
30%PU+30%MX+30%PVC+10%Cellulose+Me	1.41	2.31	0.251	0.162	0.18	0.07
100%PVC	1.67	12.9	0.110	0.334	0.07	0.03

Table XXII: Comparison of Hydrogen Cation and Chloride Extracted from Combustion Products in PAC and CG Experiments

	Entrained * Solids per Waste, g/kg		PCDD/PCDF in Gas per Waste, TEQ, ng/kg		PCDD/PCDF in Liquid per Waste, TEQ, ng/kg		PCDD/PCDF Total per Waste, TEQ, ng/kg	
	PAC	CG	PAC	CG	PAC	CG	PAC	CG
100% Cellulose	16.0	0.91	28	1.27	3.80	2.19	31.8	3.46
100% PU	9.4	0.85	19.0	14.14	13.2	1.51	32.2	15.65
100% Mixed Plastics	22.6	1.30	103	4.89	19.0	6.41	122	11.30
30%PU+60%MX+10%Cellulose	13.3	0.86	73.7	5.37	31.9	6.73	106	12.10
30%PU+30%MX+30%PVC+10% Cellulose	22.5	0.61	52.0	39.0	96	24.4	148	63.4
30%PU+30%MX+30%PVC+10% Cellulose+Me	15.4	0.36	136	1735	437	1023	1804	2758
100%PVC+Me	23.5	0.63	695	2507	64	4145	759	6651
30%PU+30%MX+30%PVC+10% Cellulose	7.0	1.20	910	169	1735	959	2646	1129
30%PU+30%MX+30%PVC+10% Cellulose+Me	16.0	0.45	272	188	1391	1447	1663	1634
100%PVC	28.4	0.47	398	82	362	870	4350	952

Table XXIII: Comparison of Polychlorinated Dibenzodioxins/Furans Extracted from Combustion

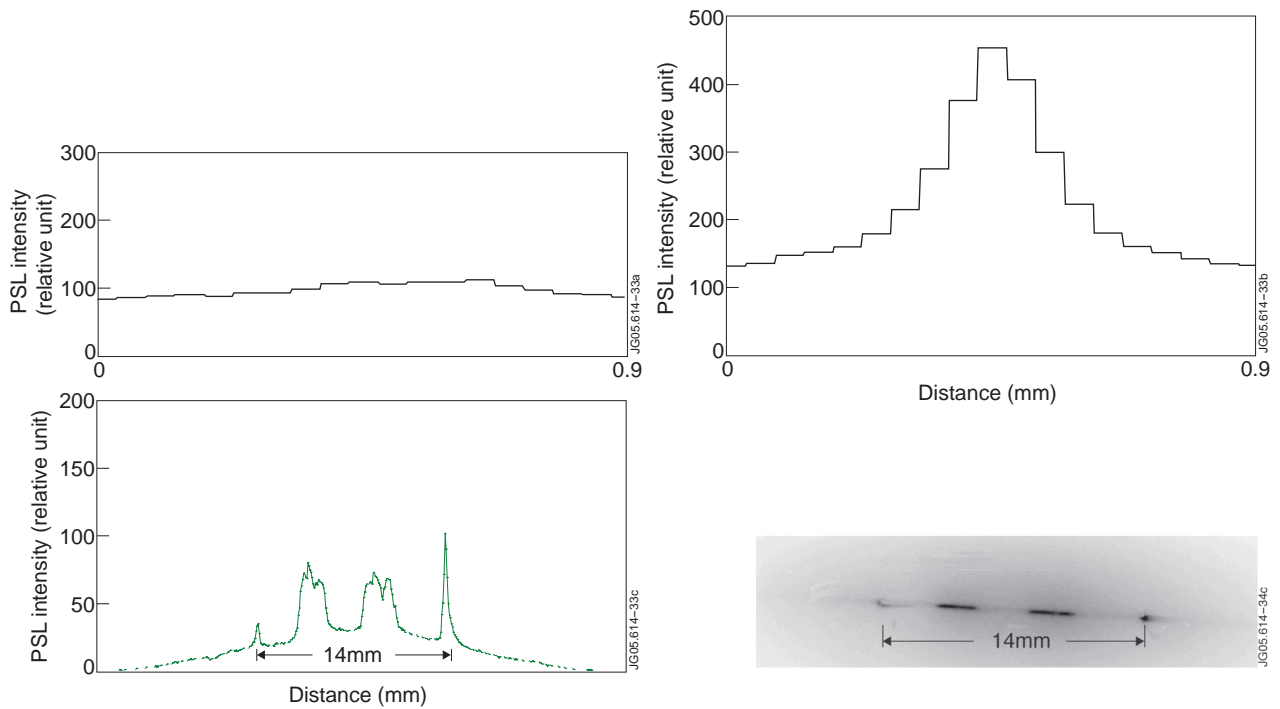


Figure :1 Tritium distribution in a sample of PVC sheet reinforced with nylon fiber and exposed to tritium for 1 hour: a) tritium depth profile measured for a cut between fibers, b) tritium depth profile measured for a cut through nylon fiber, c) tritium distribution along the surface exposed to tritium, d) image of the same surface.

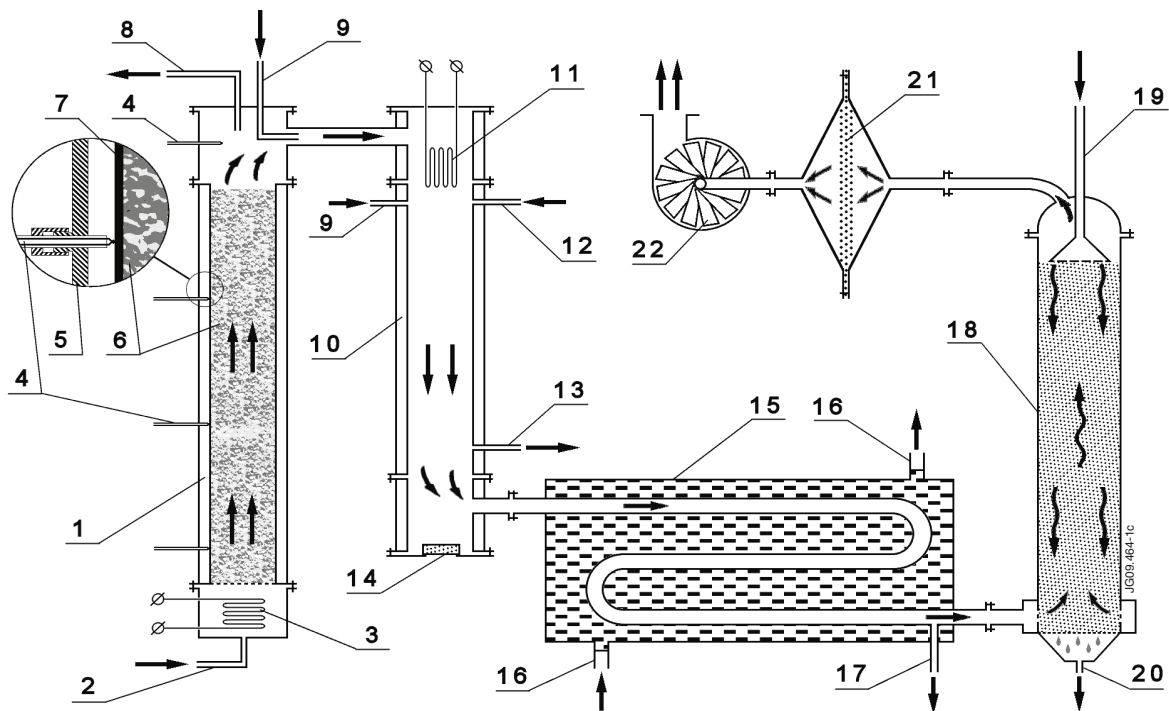


Figure 2: Process flow diagram of gasification in countercurrent regime:

(1) Gasifier reactor; (2) Primary air supply; (3) Ignition electric heater of the reactor; (4) Thermocouples; (5) Outer shell; (6) Processing mixture; (7) Refractory; (8) Product gas sampling; (9) Secondary air supply; (10) Afterburner; (11) Electric heater of the afterburner; (12) Propane supply; (13) Exhaust gas sampling; (14) Quartz window; (15) Condenser; (16) Cooling water; (17) Condensate sink; (18) Absorber; (19) Sodium carbonate solution supply; (20) Spent solution sink; (21) Filter; (22) Exhaust fan.

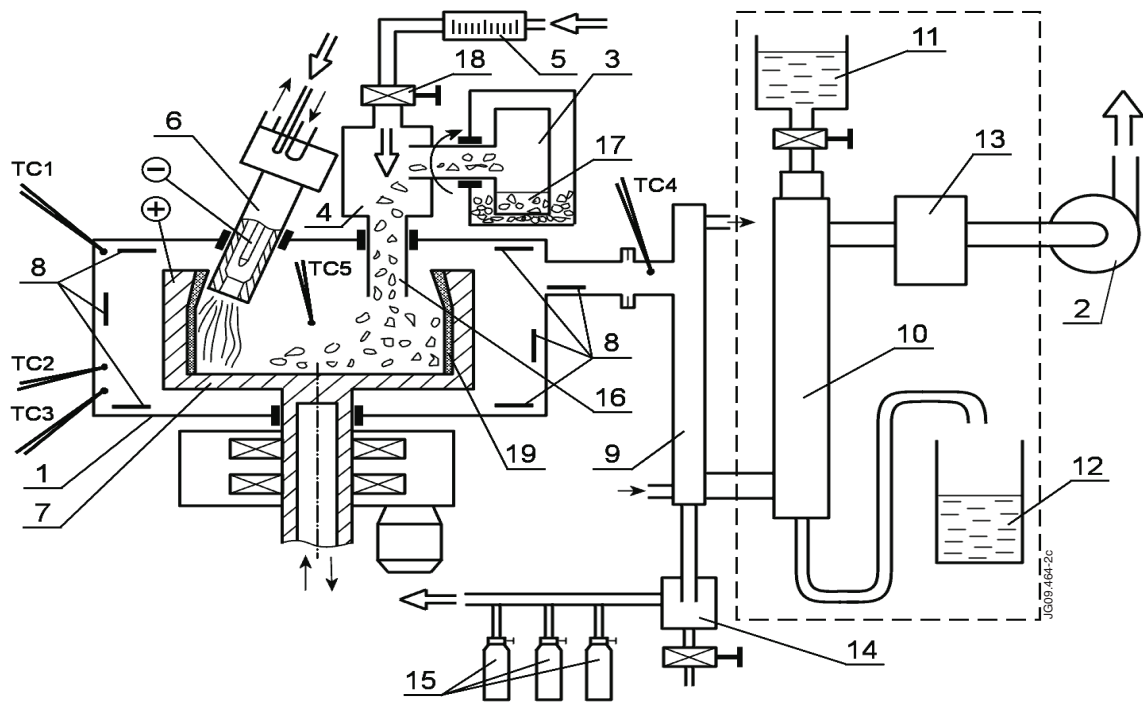


Figure 3: Process Flow Diagram for PAC Installation

(1) Hermetic Vacuum Chamber; (2) Gas Pump; (3) Metering Unit; (4) Mixing Chamber; (5) Flow Meter; (6) Plasmatron; (7) Rotating Crucible; (8) Samples for Corrosive Resistance Tests; (9) Pipe-in-Pipe Condenser; (10) Packed Filter; (11) Water Vessel; (12) HCl Collector; (13) Filter; (14) Microcyclone; (15) Ampoule Samplers; (16) Waste Feeding Pipe; (17) Transfer Scoop; (18) Control Valve; (19) Skull or Refractory Liner; TC1...TC5 – Thermocouple Locations; → Cooling Water, → Gas FlowII.