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INCINERATION OF SPENT ION EXCHANGE RESINS IN A TRIPHASIC MIXTURE AT BELGOPROCESS

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ABSTRACT

Up to 1998, spent ion exchange resins have been fed to the incinerator in combination with various other solid combustible wastes at Belgoprocess. However, thanks to sustained efforts to reduce radioactive waste production in all nuclear facilities in Belgium, the annual production of solid combustible waste is now much too small to allow this practice to be continued. Since the incinerator at Belgoprocess is not capable of treating spent ion exchange resins as such, it was decided to adopt the use of foam as a carrier to feed the resins to the incinerator. The mixture is a pseudohomogeneous charged foam, ensuring easy handling and allowing incineration in the existing furnace, while a number of additives may be included, such as oil to increase the calorific value of the mixture and accelerate combustion. The first incineration campaign of spent ion exchange resins in a foam mixture, in conjunction with other liquid and solid combustible wastes, will be started in January 2000.

INTRODUCTION

Up to 1998, spent ion exchange resins have been incinerated in combination with various other solid combustible wastes at Belgoprocess. The resins were fed in a ratio of resins to other solid wastes of 20 to 500 kg. In recent years, only part of the current production could be treated in this way. Thanks to sustained efforts to reduce radioactive waste production in all nuclear facilities in Belgium, the annual production of solid combustible waste went down to 100-130 t. As a result, the practice of mixing spent ion exchange resins with other solid combustible wastes in the incinerator feed cannot be applied continuously. Since the incinerator at Belgoprocess is not capable of treating spent ion exchange resins as such, it was decided to adopt the use of foam as a carrier to feed the resins to the incinerator.

Starting in the year 2000, most of the backlog of some 60 t of spent ion exchange resins, and the current production will be treated in the existing incineration plant at Belgoprocess, using the new feed system. The major part of the spent ion exchange resins will be incinerated at a flow rate of 50 kg/h, in conjunction with other combustible wastes, both liquid and solid. Whenever the occasion arises, spent resins and contaminated oil can be incinerated in separate campaigns, likewise using the new foam feed system.

Normally, the existing flue gas purification system suffices to eliminate all contaminating particles down to levels far below the limits imposed by the atmospheric release permit.

ORIGIN OF SPENT ION EXCHANGE RESINS

Nuclear power plants mainly use organic ion exchange resins in the treatment of their process water systems, to control the system chemistry and thereby minimise corrosion or degradation of system components, to limit the radiolysis of water and to remove radioactive contaminants.

Organic resins are also used in a number of chemical decontamination or cleaning processes for regeneration of decontamination reagents, as well as for reagent and radionuclide removal.

The ion exchange process is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solid. The solid media then becomes a radioactive waste, which must be treated adequately.

Some 30 t of spent ion exchange resins are annually produced in Belgium, the majority of which originate from nuclear power plants.

CHARACTERISTICS OF SPENT ION EXCHANGE RESINS

Most of the resins used in Belgian nuclear installations are styrene divinyl benzene copolymer mixtures, either sulphonated or containing quaternary amines, and having various ionic forms: Na, H or OH.

Spent resins are delivered in plastic bags of 15 tot 25 kg for treatment at Belgoprocess. Since 1994, resins are dried at the power stations as a pre-treatment step, reducing the water content to about 25 to 35% by weight.

The resins do not burn spontaneously and even after evaporation of the water, combustion proceeds very slowly.

Ion exchange resins contain significant amounts of sulphur and nitrogen; they are contaminated with radionuclides such as caesium and cobalt.

EARLIER PROCESSING OF SPENT ION EXCHANGE RESINS

Because the calorific value of the resins is insufficient to support self-burning, the resins were mixed with other combustible wastes in order to increase the efficiency of combustion.

Considerable quantities of resins have been processed in the former EC incinerator at Belgoprocess, partly in conjunction with solid combustible wastes, partly separately, with the additional injection of spent oil or fuel oil.

In the period 1993-95 roughly 100 t of spent resins were incinerated, in conjunction with some 500 t of other solid and liquid wastes. At the end of 1995, the EC incinerator was shut down and replaced by the new type incinerator. In the period 1996-98 only 11.5 t of spent resins have been incinerated, in conjunction with 386.6 t of other solid and liquid wastes.

In this incinerator, spent ion exchange resins were fed in packages of 15 tot 25 kg and burned together with other liquid and solid combustible wastes. In this case, there is an upper limit for the resin content. Above that upper limit, combustion is not complete.

Due to a difference in internal layout of the two incinerators, spent resins could be treated in separate campaigns in the former EC furnace, with the additional burning of fuel. Here, the burner was located near the surface where spent resins were fed, while the burner in the CILVA furnace is located in the upper part, so that the temperature at the bottom does not reach the minimum temperature of 700°C for a good combustion of spent resins.

The CILVA incinerator plant comprises the following components:

- A primary combustion chamber in which the radioactive wastes undergo a combined process of combustion and pyrolysis in a temperature range of 900-950°C.
  Solid waste is fed from the top through a water and air cooled lock system; liquids are injected in the longitudinal direction of the furnace. The floor consists of a steel grid; ashes fall through it and are removed by a double screw, extending in the longitudinal direction, to the waste drum underneath.
- A secondary combustion chamber in which unburned gases and soot particles are mixed with excess air at 1000°C to complete oxidation to primary components.
  Waste liquids can be injected from both sides in the secondary combustion chamber, in a direction perpendicular to the double screw for the removal of ashes.
- A boiler to cool down flue gases from 1000 to 200°C.
- A self cleaning sleeve filter; the removed particles being collected by a screw underneath and transferred to the connected waste drum, and HEPA filter
- A scrubbing system comprising a quencher and a counter current scrubber using caustic liquid for the removal of HCl and SO_2

Drums with ashes and dust particles are supercompacted; the pellets are loaded in 400 l drums and embedded into cement.

Purified flue gases are heated to limit condensation in the chimney. The extraction of gases and maintenance of the installation in underpressure is ensured by ventilators.

PRINCIPLE OF INCINERATION OF SOLID WASTE PARTICLES IN A TRIPHASIC FOAM MIXTURE

Resins, when fed as such to an incinerator, have the tendency to form large clusters by melting before burning, thus causing problems with the incinerator refractory as well as problems related to incomplete combustion.

Looking for an economical solution, the application of a three-phase mixture of gas, liquid and solids, in the form of a charged foam, in which each phase may contain primary waste(s) and additives, was adopted.

Advantages of the use of foams as a transport means are, among others:

- high solid/liquid ratio: a solids content in the mixture of up to 85% by weight;

- relative independence of the formulation with respect to the granulometric size distribution, composition and characteristics of the resins;
- limited contacts between particles due to the presence of air, resulting in a low viscosity as compared to the solid-liquid suspensions, and consequently only slight losses of charge during pipe transfer;
- possibility of co-incinerating other liquid or solid wastes;
- the homogeneity of the foam allows a steady combustion;
- by charging the foam with solid waste, the latter is fluidised and homogenised, thus ensuring the best possible conditions for transfer and subsequent incineration;
- pulverisation of the foam increases the surface area exposed to heat in the furnace and facilitates rapid gasification and oxidation
- the process only makes use of standard equipment (tanks, mixer, mixing/swelling apparatus, furnace).

TESTING OF PREPARATION AND INCINERATION OF TRIPHASIC FOAM MIXTURE

A feasibility study of the use of a foam carrier for the transport of resins was based on the formulation results using seven types of ion exchange resins.

As the foaming agent, a fatty ethoxylated alcohol, without sulphur and without nitrogen was chosen, taking into account the ionic forms of the resins.

Laboratory tests

Laboratory tests were carried out to determine the quality of the foam, and the effects of adding oil, ureum or lime to the foam mixture.

It was found that a good quality foam could be obtained when a given quantity of foaming solution is prepared with surfactant, and agitated to obtain a maximal swelling, before progressively adding the resins.

Oil can be included in the foam mixture to improve combustion in the primary combustion chamber, so that no burning residues are entrained by the flue gases.

If oil is added to the foaming solution prior to the resins, foams are of good quality and homogeneous, and resins may be incorporated.

Pilot tests

The continuous preparation of a charged atmospheric foam using an in-line solid/liquid/gas mixer was tested in a pilot facility, on the two most commonly used types of resin (Amberlite IR 120 and Ambersep 900 OH). The expansion rate of the foam after pumping and transfer over 30 m was slightly less than that measured at the laboratory, but the obtained values remained high

Pulverisation tests with foams charged with resins showed a
- good pulverisation with the two injection lances using additional air injection;
- blockage of the existing Belgoprocess injection lance
  The injection lance of Belgoprocess has been modified since. The nozzle diameter was increased.

No swelling problems were encountered with the various resins. Further it could be concluded that:
- there is an upper limit for the mass fraction of resins in the foams ;
- oil may be incorporated to increase the calorific value of the foam
- addition of ureum or lime destabilises the foam for certain types of resin;
- a good quality of foam can be obtained.

Incineration tests

In a pilot system in which the operating conditions of the CILVA incinerator and flue gas purification system were applied, incineration tests with representative mixtures for the spent resins of the Belgian nuclear power stations were carried out to validate injection and incineration conditions.

All foams were prepared with foaming solution containing additives, plus motor oil in foams with low calorific value. The foam mixture was injected into the pre-heated incinerator, while air was fed by a ventilator.

It was found that to obtain a good pulverisation and dispersion of the resin jet, a rapid ignition and complete combustion of the resins, it is necessary to have the correct equilibrium between the weight of resins, the foaming solution, the flow rate of charged foam and the injection of air.

The quality of foam diminished when increasing the oil content in a test to verify its effect on combustion kinetics for Na containing resins. There is an upper limit for the oil content.. The addition of oil allows a more rapid evaporation of water from the resin and an increase of its temperature. As a result the CO content is lower (better combustion), and the SO_2 content higher (more resin incinerated).

There are mixtures of foaming solutions that gave more than double NO_x contents of the flue gases as compared to the mixture without ureum. To obtain the expected effect of reducing the NO_x content, the foam should be injected in a part of the incinerator where the temperature of the gases is below an upper limit.

Conclusions of feasibility study

The following conclusions could be drawn from the feasibility study:
- there is validation of laboratory formulations for a range of flow rates;
- good combustion of various resins above a certain minimum temperature;
- calorific value of resins is very important for performance of combustion;

- incorporation of certain additives allows to improve the combustion; Na containing resin behaves more or less as the other resins;
- some additions increases NO_x content if foam is injected at flame level;
- oil may be contemplated, but it depends of the weight % of the resins.

PROCESSING OF SPENT ION EXCHANGE RESINS IN TRIPHASIC MIXTURE

In September 1999, the additional equipment for the preparation and transfer of the foam mixtures was installed in the incinerator hall at Belgoprocess.

It consists of :
- a solid storage vessel, equipped with an anti-clogging screw, from which a second vessel is fed. The latter is equipped with a screw and frequency variator to feed resins to the mixer;
- a preparation vessel with a stirrer to mix the surfactant with the water;
- a buffer vessel allowing to prepare the surfactant/water mixture in the preparation tank, while operating the foam mixer simultaneously. The buffer vessel is provided with a volumetric pump to transfer the surfactant/water mixture to the mixing vessel;
- a mixing vessel in which the foam is prepared in two steps
  it comprises an injection screw for the transport of solids, and a mixing screw in a mixing tube ensuring the production of an homogeneous, stable foam;
- liquid additives may be injected at several points into the foam, allowing to ensure that injected liquids do not disturb the foam quality
- all inlets to the foam mixer may be adjusted in accordance with the set flow ;
- a peristaltic pump, to transfer the foam to the incinerator, allowing to transport the foam without destroying it.

In 2000 this installation will be commissioned and used to incinerate the backlog of untreated resins. It further enlarge the technical capabilities of Belgoprocess in treating and conditioning radwastes.