CONTINUOUS PRECIPITATION AND FILTRATION, A PROCESS TECHNOLOGY FOR LIQUID WASTE MANAGEMENT

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ABSTRACT

The formation of a precipitate, generally followed by filtration, is a technique widely used for the decontamination of radioactive effluent. However, continuous precipitation is rarely used for waste processing. The advantages of continuous precipitation are described, as well as the importance of in-depth knowledge of this technique to cope with its difficulties. The continuous precipitation processes used by COGEMA are described and the unique advantages of this technique are outlined. The results of pilot plant tests with a surrogate of the SRS supernates are briefly described. The conclusion is that implementation of this technique will greatly help to resolve the safety issues associated with the precipitation of cesium tetraphenylborate.

INTRODUCTION

The separation of an insoluble solid is one of the more widespread technologies used for removing pollutants, either chemical or radioactive, from an aqueous waste stream. Generally, an insoluble compound is obtained by adding to the liquid waste a selected reagent that forms solid particles. This precipitation step is necessarily followed by a second step, a solid-liquid separation. The second step can be a mere settling, or a sophisticated centrifugal separation, but is usually a filtration.

Quite often, when nuclear waste is processed by precipitation and filtration, the trend is to store the waste in a tank and then to process it in steps rather than continuously. However, if there is a solid-liquid separation step in the production line of a COGEMA plant, it is nearly always continuous and designed with both continuous precipitation in a continuously stirred tank and continuous filtration.

The continuous precipitation processes used in the COGEMA plants produce excellent results. COGEMA therefore decided to assess the potential of continuous processes for managing effluent.

FUNDAMENTALS OF CONTINUOUS PRECIPITATION

Most of the properties of precipitates, including filterability, amount of residual mother liquors the cake retains and tackiness of the product on the walls of equipment, depend on the size of the precipitate particles. Control of precipitate particle size is therefore often the most important concern for the development of a precipitation process.

The performance of a precipitation process depends chiefly on the thermodynamic properties, namely, the solubility of the products. Clearly, if high performance, i. e. high decontamination factors (DF), are sought for waste processing, the formation of compounds with very low solubility must be favored.

However, the kinetics of the phenomena involved also has a major impact:

- If the precipitation is slow, it will affect mainly the residence time.
- If the precipitation is fast, the peculiarities of the precipitation kinetics will have a major effect on the overall performance of the process.

Precipitation relies on two phenomena, nucleation and growth. The concentration of nuclei rises sharply as the concentration of the product to be precipitated exceeds the nucleation threshold concentration, which is in turn greater than the solubility.

Batch operation

If these steps are fast and if the solubility is small, the batch mixing of reagents leads to a concentration of the product to be precipitated that is of the same order of magnitude as the reagents in the feed streams. For concentrations only slightly higher than the nucleation limit, the nuclei are not numerous. The number of particles is therefore low and, in turn, their size is large (typically more than some ten micrometers). However, if the reagent concentrations are high compared with the nucleation threshold concentration, the number of nuclei - and therefore the number of particles - is high. These particles are small, less than a few micrometers to well below a micrometer.

Obtaining coarse particles in a batch process will consequently only be possible by using diluted feed streams and fairly high residence times. Depending on the precipitate mass flow to be processed, large equipment can therefore be anticipated. A mitigating technique can be used: by maintaining a mild agitation of the slurry, the largest particles become larger thanks to the solubilization of the smallest ones. The rate of this step is sharply dependent on the solubility of the product. The higher the solubility, the faster the evolution toward larger and less numerous particles. Here also, highly insoluble products are clearly not suited for this process.

Continuous operation

In a certain type of continuous equipment (a well stirred tank), however, the precipitation of a highly insoluble compound with fast kinetics exhibits a very different behavior from that of a batch process. The concentrations of the reagents are low in the bulk of the tank, therefore the number of nuclei is relatively low, even though the feeds are highly concentrated. Theoretically, it is possible to process concentrated feeds in a rather small piece of equipment and to obtain coarse particles.

The adoption of a continuous process for precipitation provides unique advantages for the performance of the process: a small tank for the precipitation step, and an easier filtration step thanks to the coarse precipitates. One might therefore wonder why such processes are not widespread. One explanation is that continuous precipitation design requires precise fine-tuning since many phenomena can jeopardize the process:

- The quality of the mixing, especially for the mixing of concentrated feeds with the bulk of the mother liquors in tank. If this mixing is not strong enough, poor results may be obtained, even though the process design is sound with the only false assumption being a "perfectly stirred tank" [1].
- The design and location of the feed pipes, which is often critical, since it can lead to high local reagent concentrations, and therefore to the presence of numerous small particles making the slurry hard to filter.
- The mixing or, more precisely, the side-effects of how the mixing is performed. The quality of the mixing clearly depends on the design and velocity of the impeller. In turn, grinding of the coarse particles and foam can result from high velocities and impeller blade design.
- Other problems are occasionally encountered, frequently temperature control, since small temperature differences induce slightly different solubilities for certain compounds, which can lead to unwanted precipitation on the wall or on the impeller.

COGEMA PROCESSES BASED ON CONTINUOUS PRECIPITATION

Plutonium conversion to oxide

The most well-known COGEMA continuous process is the first step used in the production of plutonium oxide from a plutonium nitrate solution. This process, the precipitation of plutonium IV oxalate, and its technology have already been described [2], [3] (Figure 1). The solution of plutonium (typically 30 to 100 g/l) is adjusted to the tetravalent state and fed continuously, together with the oxalic acid solution, into a stirred vessel, the precipitator, where plutonium oxalate is formed. The pulp is recovered by overflow and fed into a continuous rotary drum filter (with internal feed). The precipitate is separated from the mother liquors, washed and dewatered. The suspension then falls into a screw calciner for drying and calcination before sending the oxide to the conditioning step. The process equipment is housed in glove boxes and is geometrically safe for criticality.

First used in the fifties at the UP1 plant, this process has been operational at La Hague since 1966. The MAPu facility of UP2 was revamped in the early eighties, while the T4 facility of UP3 was started in

1989. The current throughput of both facilities is 48 kg Pu/d. The R4 facility will enter service in 2001 with the same throughput, but with the capability to double it.

Since the objective of plutonium separation is to recycle plutonium for MOX fuel fabrication, this process offers unique advantages: it is continuous and yields a constant-quality PuO_2 product in terms of homogeneity, specific area, particle size, sinterability and moisture content. MOX fuel can therefore be manufactured with a well-characterized material.

Because the equipment - and especially the precipitation tank- is small, the control of criticality is easy. For the same reason, housing this equipment in a glove box of reasonable size is straightforward, which in turn enables accurate control of leaktightness.

The safety records of these facilities are excellent. The spreading of radioactive materials is prevented by a double containment system, with a cascade of pressure differentials ensuring dynamic containmentThe radioactive doses to workers have decreased to very low levels, since remote handling became routine for normal operation.

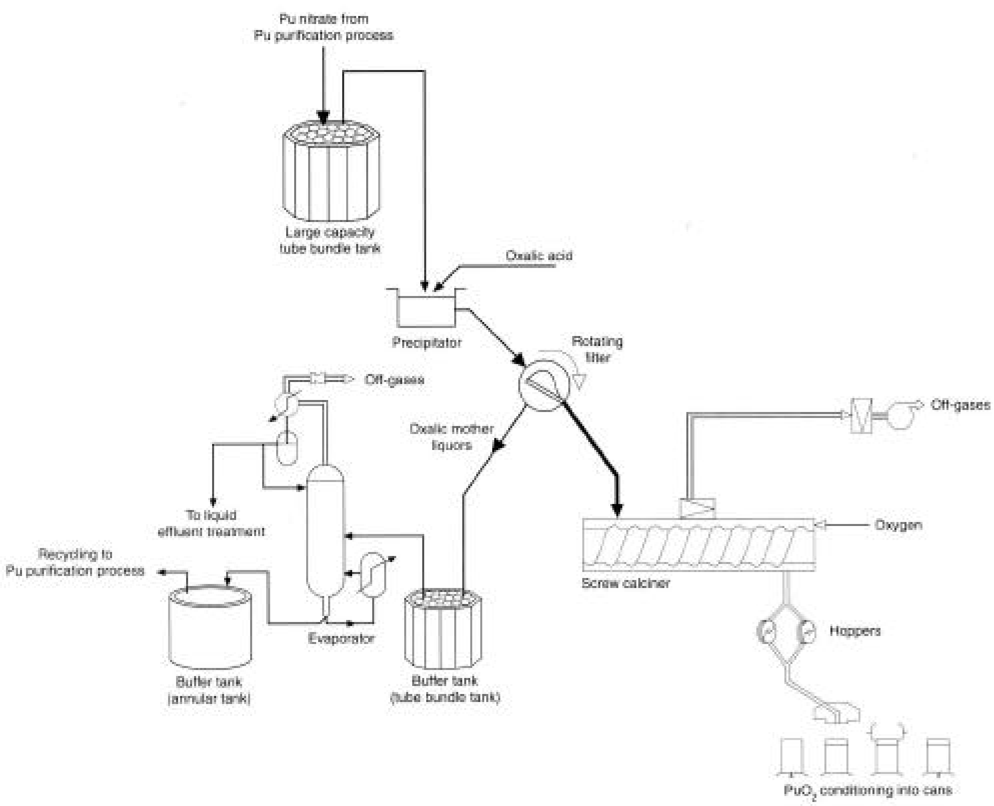

Fig. 1. Plutonium conversion by the continuous oxalate process

Uranyl peroxide precipitation

Another example of continuous precipitation use is the continuous precipitation of uranyl peroxide from a feed solution of uranium nitrate in the TU5 facility at COGEMA's Pierrelatte site [4]. The TU5 plant is dedicated to the conversion of reprocessed uranium into U_3O_8, with a maximum throughput of 1,600 t/y. At the TU5 facility, the uranyl peroxide is precipitated in an acidic medium. This new process has been selected instead of the usual alkaline precipitation, because it is far superior for management of the generated waste. The feed is a dense solution of uranyl nitrate of more than 300 g/l. After careful pilot plant testing, a design was established for the precipitation of coarse particles of uranyl peroxide. This is obtained in small equipment for such a throughput: a set of 200-liter stirred tanks. The facility has been operating since 1995.

APPLYING CONTINUOUS PRECIPITATION TO WASTE MANAGEMENT

The Savannah River Site initiated a cesium decontamination process for the supernates via cesium tetraphenylborate precipitation. This facility, which relied on batch precipitation of cesium and potassium tetraphenylborate, has been shut down due to the unexpected release of benzene [5]. However, the capability of the sodium tetraphenylborate as a reagent to decontaminate the supernate from cesium has been confirmed.

To demonstrate the validity of continuous precipitation for waste management, COGEMA decided to conduct pilot plant tests on a surrogate of supernates containing caustic soda, sodium, potassium and cesium nitrate in the average proportions of the actual waste. The tests were performed in a continuously fed stirred tank of significant size (about 200 liters).

These tests have shown that potassium and cesium are simultaneously precipitated with a high yield: the ratio of soluble potassium before precipitation, compared to the one after precipitation is $> 2.5\ 10^3$, and the ratio of soluble cesium before precipitation, compared to the one after precipitation is $> 3.5\ 10^2$. These figure are limited by analytic accuracy and not by insufficient precipitation (as demonstrated by laboratory scale tests spiked with radioactive cesium). The more striking result is the following: by continuous precipitation with residence times less than one hour, coarse particles are obtained and their average size is well over 20 µm, while with batch precipitation performed in similar conditions (concentrations of reagents, temperature, etc…), small particles less than 1 µm are produced.

We have checked that cross-flow ultrafiltration is not necessary to separate these particles from the mother-liquors and that metallic clothes with a 16 µm clearance are sufficient for this separation. This allows us a wide choice of filters, including continuous filters already developed and used by COGEMA, including designs with short residence times, both for solids and liquids flows.

The results show that the safety issues associated with cesium tetraphenylborate precipitation can be resolved by using continuous precipitation, because the residence times are short and, thanks to mixing, the temperature can be kept under control:

- Continuous precipitation and filtration prevent most of the formation and accumulation of benzene by the combination of short residence time and controlled low temperature.
- The containment of the small amount of benzene, which may be produced is easy to implement, due to the small size of equipment.

CONCLUSION

Continuous precipitation is a powerful tool for the nuclear industry and especially for waste processing, but this technology must comply strictly with a full set of design rules. Experience is therefore invaluable to design such a process. COGEMA has developed and is using several continuous precipitation processes in its plants, especially for plutonium and uranium conversion to solid state. Tests have confirmed that this technique can be used for waste processing, with the same outstanding advantages as for conversion, i. e. process and safety advantages but also the possibility to use currently available efficient technologies that are well suited to the nuclear industry, such as those used for ensuring leaktightness and easy maintenance.

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