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INTRODUCTION

The Savannah River Plant (SRP) temporarily stores high-level radioactive waste in underground storage tanks. Approximately 2.85×10^5 cubic meters of waste have evaporated to 1.15×10^5 cubic meters since plant startup in the early 1950's. Sixty percent of the radioactivity is contained in the approximate 10 volume percent stored as alkaline sludge. The remainder of the waste and radioactivity is stored as alkaline salt cake and salt solution. The waste management process development objective for permanent disposal is to concentrate the radioactivity into the smallest practical volume.

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Starting in 1989, the Defense Waste Processing Facility (DWPF) will begin incorporating the salt and sludge radionuclides into borosilicate glass. The glass will be contained in stainless steel canisters and ultimately stored in a Federal geologic repository. The DWPF is a remotely operated chemical processing and vitrification plant.[1] The volume of waste that must be processed is directly related to the cost of the DWPF. Great gains in volume reduction have been made with the large salt fraction of the waste.

Greater than 99% of the radioactivity in 15-year aged salt is from cesium-137 and strontium-90.[2] A process combining precipitation, adsorption, and filtration has been developed to concentrate the cesium and strontium into 1/10 the volume of the saturated salt solution. This concentrate and the alkaline sludge are the two radioactive feed streams to the DWPF. The remaining 9/10 of the salt waste is essentially decontaminated and is treated as a low-level hazardous waste. Inside the DWPF the concentrate is further processed to minimize the downstream volumes required to vitrify the radionuclides into borosilicate glass. The chemical and engineering aspects of these volume reduction operations are described in this paper.

SALT DECONTAMINATION PROCESS

The objective of the Salt Decontamination Process is to decontaminate the largest practical volume of SRP salt waste by concentrating the primary radioactive compounds. This batch process is performed in existing underground storage tanks having a nominal working volume of 5×10^3 cubic meters (1.3 million gallons). Sodium tetraphenylborate (NaTPB), sodium titanate, and crossflow (tangential) filtration are the key components of this process.

SRP high-level waste salt cake is dissolved to form an alkaline solution saturated in sodium salts (Figure 1). This solution is transferred to a batch processing tank. Recycled wash water (described herein) is added to the solution to dilute the sodium ion concentration. A solution of NaTPB and a slurry of sodium titanate particles are added to the waste. Potassium and cesium react with the NaTPB to form precipitates of potassium tetraphenylborate (KTPB) and cesium tetraphenylborate (CsTPB). Excess NaTPB precipitates also. Strontium and plutonium are adsorped by the sodium titanate particles. The solids, now containing the radioactivity, are concentrated by crossflow filtration. The decontaminated filtrate is mixed with cement and aggregate to form saltstone for stable disposal.[3] The concentrate is washed and filtered again to reduce the soluble

salt content and to dissolve the excess NaTPB. The filtered wash water is recycled and used to dilute the saturated salt solution of the next batch. The dissolved NaTPB is used for precipitation once again. Washed and concentrated precipitate slurry is pumped to a storage tank to await feeding to the DWPF.

PRECIPITATION CHEMISTRY

Sodium tetraphenylborate [$NaB(C_6H_5)_4$] is soluble in water to 0.9 molar. The other alkali metals and some of the transition elements form highly insoluble salts of tetraphenylborate in aqueous solutions. (The precipitation of potassium tetraphenylborate is an analytical method for determining potassium concentrations in aqueous solutions.[4]) The SRP alkaline waste salt solution consists primarily of sodium hydroxide, nitrate, nitrite, sulfate, aluminate, and carbonate. A saturated salt solution has an average sodium ion molarity of 6.9 and is 37 wt % salt. The potassium and cesium molarities in this solution are 3.1×10^{-2} and 2.5×10^{-4}, respectively.[3] The challenge is to precipitate the cesium with tetraphenylborate so that the dissolved cesium concentration in the filtrate is reduced to less than 2.5×10^{-8} molar (from approximately 30 ppm cesium to less than 0.003 ppm cesium).

Cesium precipitation is affected by the sodium and potassium ion concentrations, the amount of excess NaTPB, and the contact time. As the sodium concentration increases, the CsTPB and NaTPB solubilities decrease. This helps remove dissolved cesium from solution, but is also slows the rate of CsTPB formation due to the low NaTPB solubility. In the average SRP salt solution, the NaTPB solubility is given by:

$$[NaTPB] = 0.923 \times e^{-1.23[Na+]}$$

where $[Na^+]$ is the sodium ion molarity excluding NaTPB.[5]

The presence of potassium (125:1 mole ratio K:Cs) and use of excess NaTPB allows for the coprecipitation of Cs/K/NaTPB. The dissolved cesium can be reduced by orders of magnitude in a reasonable amount of time by balancing the potassium, sodium, and excess NaTPB concentrations. For the SRP Salt Decontamination Process the salt solution is diluted to a sodium molarity of 5.0, the NaTPB excess added is equivalent to 60% of the amount required for stoichiomteric potassium precipitation, and the time allowed for precipitation is two days. The resulting decontamination factor (DF) for cesium is greater than 10^4. The DF is a number used to quantify the extent of radionuclide removal for a particular process. For this process DF is defined as:

$$DF = \frac{\text{Concentration in the Feed Solution}}{\text{Concentration in the Filtrate Solution}}$$

ADSORPTION CHEMISTRY

Sodium titanate ($NaTi_2O_5H$) is a white, finely divided solid that adsorbs strontium and plutonium. It is added to the salt waste as a slurry along with the NaTPB. Soluble strontium is present in the salt waste as Sr^{+2} at approximately 5×10^{-7} molar. Plutonium is present as both dissolved and particulate species. The adsorption process is an ion exchange reaction approximately represented by the following stoichiometry:

$$Sr^{+2}_{(aq)} + 2NaTi_2O_5H_{(s)} + 2OH^- = 2H_2O + Sr(NaTi_2O_5)_{2(s)}$$

$$Pu^{+4}_{(aq)} + 4NaTi_2O_5H_{(s)} + 4OH^- = 4H_2O + Pu(NaTi_2O_5)_{4(s)}$$

The DF's for strontium depend on the amount of sodium titanate added, the initial strontium concentration, and the contact time.[5] A strontium DF of 200 can be obtained by adding 0.5 g sodium titanate per liter of salt solution with two days of contact. The plutonium DF is a function of filtration and adsorption. Filtration after one day in the presence of sodium titanate can yield a plutonium DF of 500.

FILTRATION

Crossflow filtration concentrates the solids after the precipitation and adsorption reactions are completed. SRP uses commercially available filters made of sintered metal tubes

arranged in a shell and tube heat exchanger configuration. The slurry is fed through the tubes, and the filtrate weeps through the pourous metal membrane into the shell. Filtrate is collected in small hold tanks and is sampled to ensure decontamination prior to transfer to a storage tank. The concentrate is recycled to the processing tank and passed through the tubes again and again. A backpulse momentarily reverses the filtrate flow at a regular interval to maintain high average filtrate rates. This backpulse is short, sharp, and sufficiently higher in pressure than the tube side to ensure adequate solids removal from the tube walls and the pores (Figure 2).

Pressure drop across the filter membrane was identified as the primary variable controlling the filtrate flux (filtrate rate/filter area) for the SRP conditions. The higher the pressure drop the better the initial filtrate flux. As processing continues, the filtrate flux descreases as solids collect on the tube wall. Very high pressures can force the precipitate into the pores and permanently clog the filters. It was found that a pressure drop of 20 to 30 psi across the filters with a backpulse pressure drop of 50 psi gave high average filtrate fluxes for long periods of time. A 0.5-micron average pore size was shown to be preferable over 0.2- and 2.0-micron filters. The 2.0-micron filter allowed some solids to pass through, and the 0.2-micron

filters had unacceptable filtrate fluxes. Extensive testing with the 0.5-micron filters gave excellent DF's and filtrate fluxes for a wide variety of conditions.[3] Figure 3 shows the effect of backpulse, filtration time, and precipitate concentration on typical crossflow filtration at SRP.

During the filtration process the precipitate slurry is concentrated from about 1.0 wt % insoluble solids to 10 wt %. Once the precipitate is concentrated to 10 wt %, process water is added to wash out the soluble sodium salts and to redissolve the excess NaTPB. (The primary waste management objective is to get the radioactive elements into stable borosilicate glass in the DWPF and to keep the nonradioactive elements in the glass to a minimum.) To conserve on wash water this is carried out as a continuous wash. Wash water is added at approximately the same rate filtrate is removed. As a result, the majority of the filtration is performed at the 10 wt % solids concentration.

Use of a low shear pump is necessary to maintain high filtrate fluxes at high solids concentrations. The precipitate flocs are easily sheared and can clog the filters. A recessed impeller centrifugal pump has been developed that improves the filtrate flux by a factor of 7 over a conventional centrifugal pump when processing 10 wt % precipitate slurry. Only 10 to 20% of the

precipitate contacts the low shear pump impeller. Given time, the sheared precipitate will reform larger flocs. (The residence time in the processing tank between filter passes is about 15 hours.) The concentrated and washed tetraphenylborate/sodium titanate slurry contains virtually all of the radionuclides in the saturated salt solution, but represents only 1/10 the original volume.

DWPF PRECIPITATE HYDROLYSIS PROCESS

Prior to incorporating the radionuclides into borosilicate glass, the concentrated precipitate undergoes hydrolysis in the DWPF. This process removes over 90% of the tetraphenylborate aromatic hydrocarbons ($C_6H_5^-$) from the radionuclide stream.

Vitrification of radionuclides into borosilicate glass is performed in a glass melter operated around 1,100°C.[1] At this high temperature the cations are reduced to oxides and incorporated into the glass matrix. Most of the anions and all the hydrocarbons are oxidized and carried out through the off-gas system. For each mole of $C_6H_5^-$ oxidized, approximately 7.5 moles of oxygen are required and 9 moles of gas are generated. By removing the aromatic compounds prior to feeding the melter, the amount of oxygen required and the size of the off-gas system can

be minimized. The aromatic compounds form their own separate benzene-rich phase. This phase is decontaminated so it can be destroyed outside the heavily shielded DWPF vitrification building in a low-level hazardous waste incinerator.

Figure 4 is a flow diagram of the batch DWPF Precipitate Hydrolysis Process. The reactor is operated semibatch. Formic acid and copper catalyst are added to the reactor containing about 25% of the aqueous product from the previous batch. This reactor solution is heated to 90°C. The concentrated precipitate is fed into the reactor at a controlled rate over a period of one hour. As the precipitate enters the hot agitated solution, it is diluted and begins to undergo hydrolysis. Benzene and other aromatic compounds are produced. Benzene (n.b.p. 80.1°C) flashes out of the 90°C reaction mixture. Once all the precipitate has been fed, the reaction mixture is heated to its aqueous boiling point of 102°C.

Vapors from the reactor are condensed into two phases. The condensed phases are separated in a decanter. The aqueous phase is recycled to the reactor, and the organic phase flows to the evaporator at ambient temperature. Boiling continues in the reactor to allow the hydrolysis reactions to approach completion and to steam-strip higher boiling aromatic compounds from the aqueous phase.

Once the reaction and batch distillation are completed, the organic phase is decontaminated in the evaporator. By washing the organic phase (> 90 wt % benzene) with water, cesium is extracted from the organic phase into the water. The evaporator is then heated to boil away the benzene. This is followed by aqueous boiling to once again steam-strip the higher boiling aromatic compounds. The vapors are condensed and decanted in a separate but identical condenser/decanter as used with the reactor. The organic phase flows to a condensate tank, and the aqueous phase is returned to the evaporator. Organic contamination is due to contact with the contaminated aqueous phase. No volatile cesium compounds are produced by the reactions. The organic in the condensate tank is sampled to ensure decontamination. The clean organic is pumped outside the shielded DWPF and held for incineration. If the organic were to be contaminated, it could be recycled to the evaporator before exiting the building and the decontamination process repeated.

The aqueous product from the reactor contains less than 10% of the original aromatic compounds and virtually all the radioactivity. It is blended with high-level waste sludge within the DWPF. Excess water is evaporated and glass-forming frit is added. The concentrated sludge is about 45 wt % total solids and is fed to the glass melter for vitrification. The amount of

aromatic carbon fed to the melter in this slurry is within the limits of the melter off-gas system.

REACTION CHEMISTRY

Tetraphenylborate precipitates decompose in aqueous acidic solutions and are converted to triphenylboron and benzene. Triphenylboron then undergoes hydrolysis to phenylboric acid and benzene.[4] Phenylboric acid is stable in aqueous solutions below 150°C, except in the presence of certain metal catalysts. Phenylboric acid is then cleaved to form boric acid and benzene. Copper(II) has been found to be an effective catalyst to cleave phenylboric acid at 100°C. Investigations by Savannah River Laboratory (SRL) and others[6] have not found a more efficient catalyst than copper(II). The catalyst also increases the reaction rates of the tetraphenylborate and triphenylboron reactions. The stoichiometry for the above reaction is:

$$B(C_6H_5)_4^- + H^+ \rightarrow B(C_6H_5)_4 + C_6H_6$$

$$B(C_6H_5)_4 + 2H_2O \rightarrow C_6H_5B(OH)_2 + 2C_6H_6$$

$$C_6H_5B(OH)_2 + H_2O \xrightarrow{Cu^{+2}} B(OH)_3 + C_6H_6$$

Tetraphenylborate and triphenylboron react completely, and the phenylboric acid reacts to about 85 to 90% completion. The sodium titanate is unaffected by the hydrolysis. Any desorption of radionuclides is of no consequence once the salt solution was decontaminated.

Formic acid was chosen for acidifing the precipitate because it does not provide an anion to substitute onto the benzene ring. Benzene's high vapor pressure makes it easier to separate from the aqueous phase by batch distillation than chloro-, nitro-, or sulfo-substituted aromatic compounds with lower vapor pressures. Formic acid is also compatible with downstream DWPF chemical processing operations.[1]

The large variety of dissolved salts remaining in the precipitate feed contribute to side reactions occurring during the hydrolysis reactions. Nitrogen-containing aromatic compounds are formed due to the reaction of nitrite with formic acid to produce a weak nitrous acid (HNO_2) solution. The nitrite also undergoes oxidation-reduction reactions with formic acid. Oxidation reactions influence the production of phenol (C_6H_5OH), biphenyl $(C_6H_5)_2$, and terphenyl $(C_6H_5)_3$.[7] These byproducts all have normal boiling points greater than 100°C. As a result, the aqueous solution requires a prolonged steam-stripping (boiling) cycle to remove these aromatic compounds and transfer them to the organic phase in the decanter.

REACTION ENGINEERING

Statistically designed experiments were used to develop the Precipitate Hydrolysis Process operating conditions. High aromatic removal from the aqueous phase and a smooth reaction profile were the response variables. Catalytic cleaving of phenylboric acid [$C_6H_5B(OH)_2$] with copper improved the aromatic removal from an unacceptable 75% to an acceptable 90%. The overall reaction rate increase with the use of copper led to the development of a reactor feeding method that does not require a pressure vessel to contain foam.

The concentrated tetraphenylborate precipitate easily traps gases and forms a stable foam. Heating of the precipitate causes dissolved gases to be expelled from solution, but they can be trapped by the precipitate to form foam. The nitrite-formic acid reaction produces NO_x and CO_2, which are also trapped by the precipitate. When formic acid is added to the precipitate and then the mixture is heated to reaction temperatures (100°C), the foam layer more than doubles the apparent volume of the solution. To contain this foam a pressure vessel was used as a reactor. This vessel was sealed prior to heating and reopened only after the hydrolysis reactions had occurred and the foam was destroyed.

Foaming is eliminated by feeding the precipitate into the formic acid/copper catalyst solution at the hydrolysis reaction

temperature. Upon feeding the precipitate is diluted and reacts readily to destroy the foam causing tetraphenylborate. Hydrolysis is not complete for a significant time later, but the intermediate compounds do not support foam. The copper is required to achieve the faster reaction rates. Foam is still produced by this method when no catalyst is used. Without the foam problem an ambient pressure reactor is used.

BATCH DISTILLATION AND ORGANIC DECONTAMINATION

The reactor feeding temperature is 90°C. Benzene (n.b.p. 80.1°C) flashes from the reactor as it is generated. Once all the precipitate has been added, the reaction temperature is raised to aqueous boiling (100 to 102°C). The hydrolysis reactions proceed towards completion, and higher boiling aromatic compounds are steam-stripped. The decanter allows gravity phase separation and recycle of the aqueous phase to the reactor. Organic is removed by gravity overflow to the evaporator to await decontamination. At the end of the steam-stripping cycle, the acidic aqueous phase in the reactor contains the radionuclide, sodium, potassium, and boron salts and less than 10% of the aromatic hydrocarbons originally comprising the precipitate.

No volatile cesium compounds are formed during the hydrolysis reactions. Cesium conamination of the organic phase is through

entrainment of aqueous phase during boiling from the reactor. Clean water is added to the organic phase in the evaporator to extract the entrained cesium. A second batch distillation is done in the evaporator to separate the organic phase from the contaminated water. Both the reactor and evaporator are operated half-full with a low boiling flux and have an impingement plate at the entrance to the vapor line leaving the vessel. Cesium is normally not considered soluble in benzene. The organic phase contains formic acid, water, and other compounds that may enhance the solubility. Double evaporation and extraction reduce the cesium concentration to the parts-per-trillion level. The benzene-rich organic phase is treated as a low-level hazardous waste.

CONCLUSIONS

In 1983 approximately 1.6×10^3 cubic meters (427,000 gallons) of radioactive salt solution were decontaminated in a full-scale demonstration. The cesium DF was in excess of 4×10^4 vs. a goal of 1×10^4.[9] Data from this test were combined with pilot data and used to design the permanent facilities currently under construction. Startup of the Salt Decontamination Process is scheduled for 1987 and will decontaminate 2×10^4 cubic meters (5.2 million gallons) of

radioactive salt solution and generate 2×10^3 cubic meters (520,000 gallons) of concentrated and washed precipitate per year.

The DWPF will begin processing this concentrate in the Precipitate Hydrolysis Process starting in 1989. Laboratory data using simulated salt solution and nonradioactive cesium are being used to design this process. A 1/5-scale pilot plan is under construction and will be used to gain large scale operating experience using nonradioactive simulants. This pilot plan is scheduled to startup in early 1987.

The incentives to reduce the volume of waste that must be treated are self-evident. At Savannah River process development innovations to minimize the DWPF feed volumes have directly improved the economics of the process. The integrity of the final borosilicate glass water form has not been compromised by these developments. Many of the unit operations are familiar to chemical engineers and were put to use in a unique environment. As a result, tax dollars have been saved, and the objective of safely disposing of the nation's high-level defense waste has moved forward.

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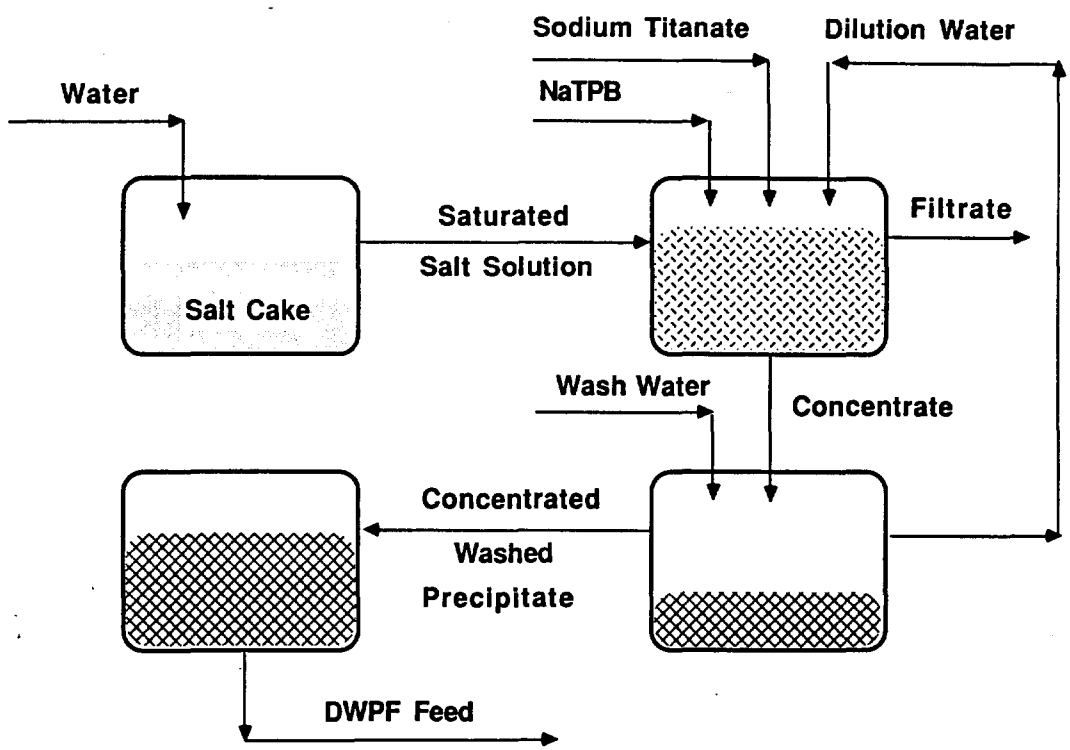

Figure 1. Salt Decontamination Process

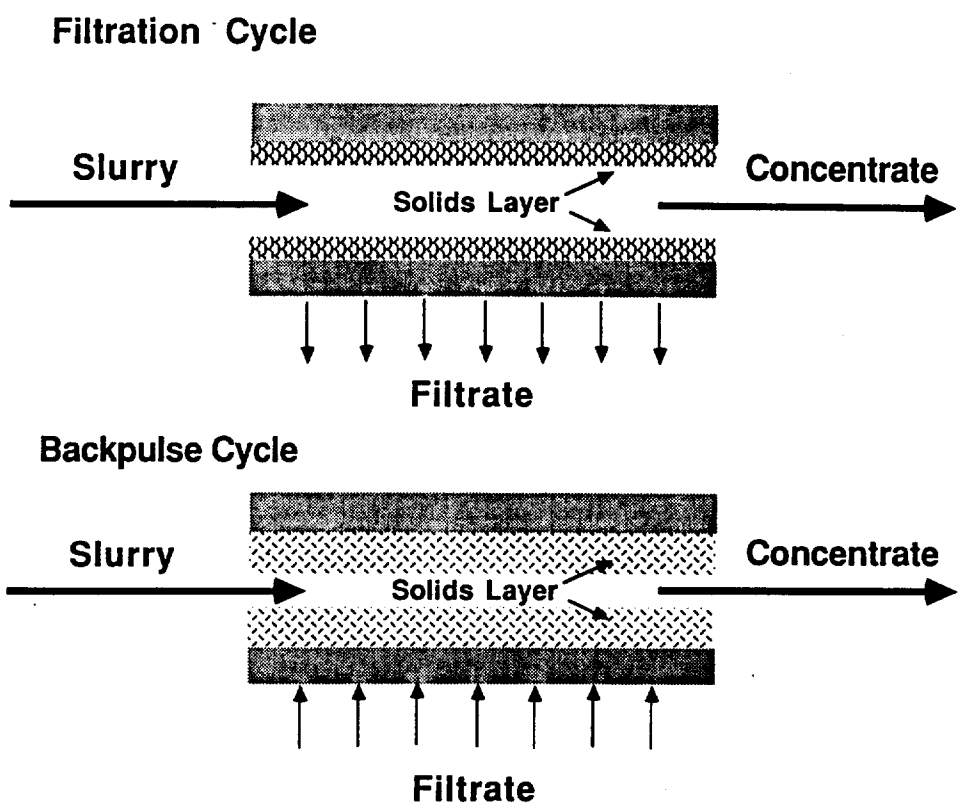

Figure 2. Crossflow Filtration and Backpulse Comparison

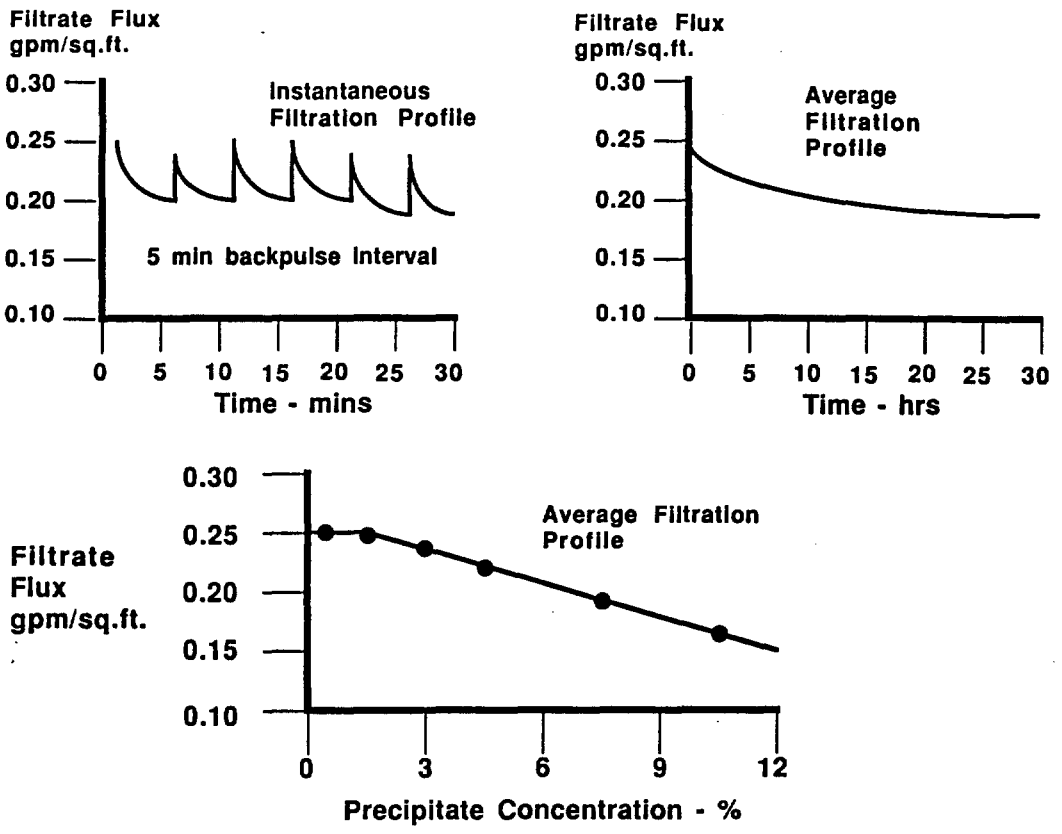

Figure 3. Typical Crossflow Filtration Profiles

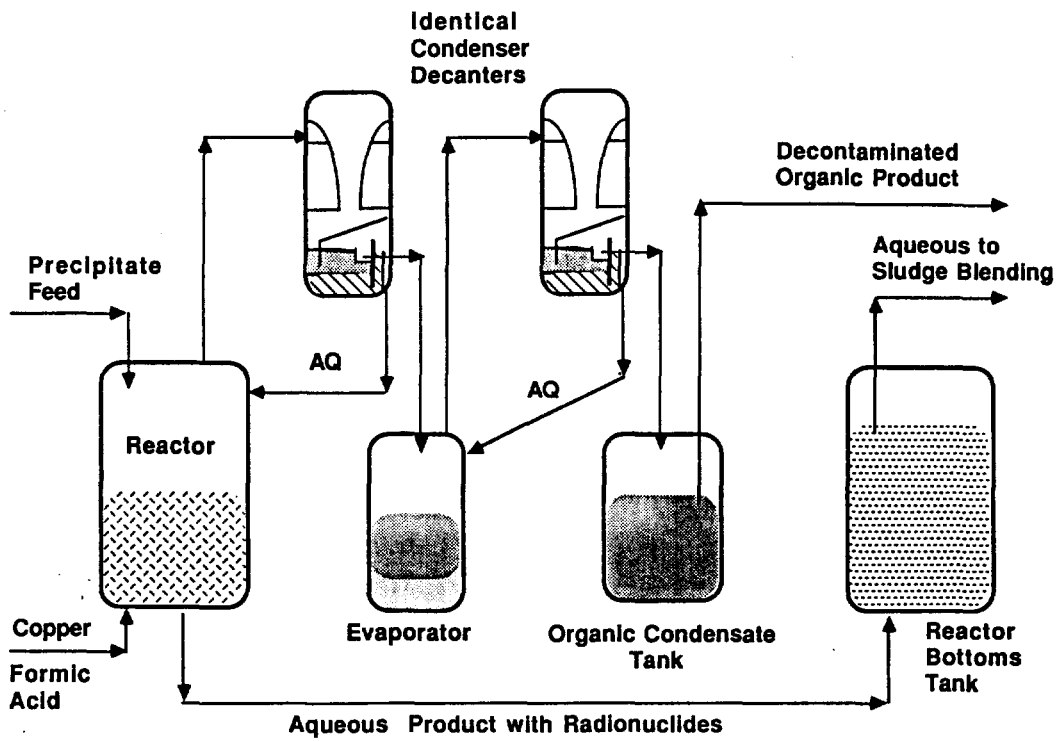

Figure 4. DWPF Precipitate Hydrolysis Process