Development of Concentration and Calcination Technology For High Level Liquid Waste

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ABSTRACT

The concentrated medium and high-level liquid radio chemicals effluents contain nitric acid, water along with the dissolved chemicals including the nitrates of the radio nuclides. High level liquid waste contain mainly nitrates of cesium, strontium, cerium, zirconium, chromium, barium, calcium, cobalt, copper, nickle, iron etc. and other fission products. This concentrated solution requires further evaporation, dehydration, drying and decomposition in temperature range of 150 to 700 deg. C. The addition of the calcined solids in vitrification pot, instead of liquid feed, helps to avoid low temperature zone because the vaporization of the liquid and decomposition of nitrates do not take place inside the melter. In our work Differential and thermo gravimetric studies has been carried out in the various stages of thermal treatment including drying, dehydration and conversion to oxide forms. Experimental studies were done to characterize the chemicals present in high-level radioactive waste.

A Rotary Ball Kiln Calciner was used for development of the process because this is amenable for continuous operation and moderately good heat transfer can be achieved inside the kiln. This also has minimum secondary waste and off gases generation. The Rotary Ball Kiln Calciner Demonstration facility system was designed and installed for the demonstration of calcination process. The Rotary Ball Kiln Calciner is a slowly rotating slightly inclined horizontal tube that is externally heated by means of electric resistance heating. The liquid feed is sprayed onto the moving bed of metal balls in a slowly rotating calciner by a peristaltic type-metering pump. The vaporization of the liquid occurs in the pre-calcination zone due to counter current flow of hot gases. The dehydration and denitration of the solids occurs in the calcination zone, which is externally heated by electrical furnace. The calcined powder is cooled in the post calcination portion.

It has been demonstrated that the Rotary Ball Kiln Calciner can be used for calcination of high-level radioactive waste. The calcined product is consistent and uniform. The operation has been further optimized by on line data acquisition system. The results of laboratory studies and experimental results and design and operation of a demonstration plant are described in this paper.

INTRODUCTION

The medium and high-level liquid radio chemicals effluents are concentrated by Thermosyphon Evaporators. The evaporation of liquid beyond 20-30% chemical concentration results in excessive fouling of the evaporator tubes. The concentrated liquid contains nitric acid, water along with the dissolved chemicals including the nitrates of the radio- nuclides. These concentrated solutions require further evaporation, dehydration, drying and decomposition in temperature range of 150 to 700 deg. C. In the Calcination process, remaining water and nitric acid are evaporated and the concentrated slurry is dried. The dry solids are dehydrated and on further heating the nitrates are transformed into oxides. The oxides produced by calcining the waste are chemically stable and compatible with the glass matrix. Increasing concern for optimum design and operation parameters in this processes have stimulated research, and step-by-step investigations. In our work Differential and thermo gravimetric studies has been carried out in the various stages of thermal treatment including drying, dehydration and conversion to oxide forms [1]. The experimental results and design and operation are described in this report.

The reduction processes of calcination are used in several chemical process plants for reduction of salts into their oxides. While concentrating the radioactive liquid waste in the evaporators with increase in concentrations beyond 20% it has been observed that the kinetics of scale formation and fouling increases rapidly. It is necessary to develop an intermediate process for evaporation of the remaining liquid, dehydrate and denitrify the chemicals prior to vitrification. The nitrates are water-soluble and corrosive; the oxides produced by calcining the waste are granular, chemically stable with good heat conductivity and compatible with the glass matrix. The addition of the calcined solids in vitrification pot, instead of liquid feed, helps to avoid low temperature zone because the vaporization of the liquid and decomposition of nitrates do not take place inside the melter.

A study was embarked to characterize the chemicals present in high-level radioactive waste. The Rotary Ball Kiln Calciner was selected for development of this process because this is amenable for continuous operation and moderately good heat transfer can be achieved inside the kiln [2]. This will also have minimum secondary waste and off gases. A Rotary Ball Kiln Calciner was designed and installed for demonstration of calcination process. The Rotary Ball Kiln Calciner is a slowly rotating slightly inclined horizontal tube that is externally heated by means of electric resistance heating. The liquid is fed sprayed onto the moving bed of metal balls in a slowly rotating calciner by a peristaltic type-metering pump. These balls crush the lump forms during calcinations; also provide extended heat transfer area. Initially dry test runs were conducted to test the rotary calciner system - the thermal inertia and no load heat requirements were recorded. The vaporization of the liquid occurs in the pre-calcination zone due to counter current flow of hot gases. The dehydration and denitration of the solids occurs in the calcination zone, which is externally heated by electrical furnace. The calcined powder is cooled in the post calcination portion. The calcined product is consistent and uniform. The rates of heating during dry test runs and during vaporization of water were tested - the steady state temperatures inside the calciner system were recorded. The test runs were carried out for optimizing the process parameters at different process condition, blank test runs were taken at different rpm, and at different set temperatures, test runs with water were also taken to study the heat transfer. Ultimately the calciner was tested for strontium nitrate solution.

NEED FOR CALCINATION

The thermal energy requirement for the various processes, during direct vitrification in the glass melter, per unit volume of the concentrated liquid feed, for typically waste containing 30% nitrate salts; is 65 % for evaporating the concentrated liquid feed; this includes heating and latent heat of evaporation and decomposition of nitric acid in the temperature range 25 to 125 ^{0}C; 31% heat is required for decomposing the glass slurry and waste nitrate into their corresponding oxides in the temperature range 125 to 700 ^{0}C. And only 4% heat required for glass vitrification in the temperature range of 700 to 1000^{0}C. This is also shown in Fig.-1. Therefore, it will be always prudent to carry out the low temperature, high enthalpy and energy intensive processes of evaporation, dehydration and calcinations in separate intermediate Equipment. And the addition of dried, calcined solid into the melter instead of liquid feed will help to avoid low temperature zones and thermal cycling and mechanical stress of melter. This will also reduce the heat load and operational difficulties due to swelling, foaming, frothing and significantly reduce the generation of very high off-gas volumes, associated with high entrainment and secondary waste.

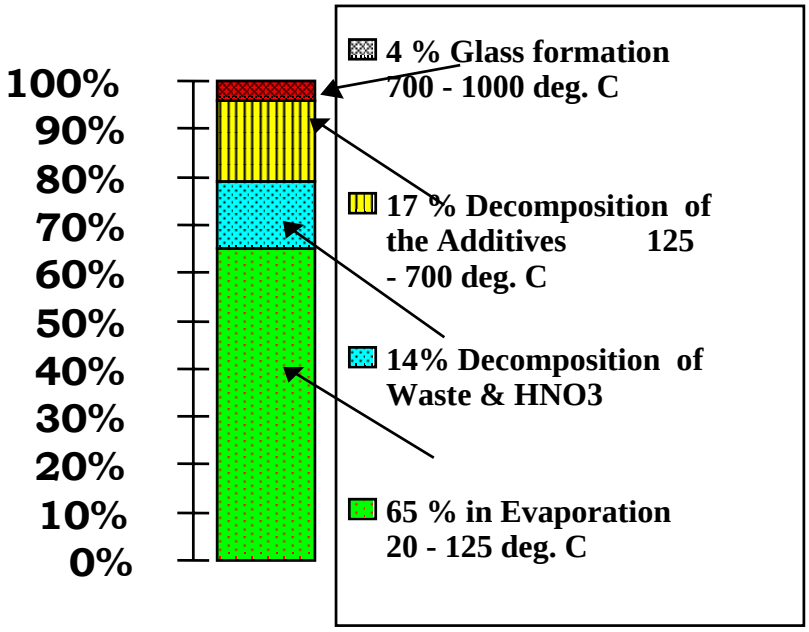

Fig. 1. Thermal energy in volume reduction processes

CALCINATION STUDIES OF CHEMICALS PRESENT IN H.L.L. W ASTE

Batch Calcination was done to find weight loss during dehydration and de-nitration process. High temperature three phase electrical resistance heated furnace of 9 kw with Chromel-Alumel thermocouple with ± 2ºC. controllability up to 1000ºC. Samples of nitrates about three gms were heated in refractory crucibles, three samples taken at a time to check any experimental error. Weight loss due to denitration was measured and percentage residual weight was calculated.

Cesium nitrate

The stoichiometric residual weight percent for conversion of $CsNO_3$ to Cs_2O_3 and Cs_2O are 80.5 weight% and 72.2% respectively. In our experiment during TGA the weight loss for Cs NO_3 started at 580°C and complete loss of weight occurred at 860°C suggestive of decomposition and conversion to oxide form. In batch calcinations studies the residual weight percent was 82% at 800°C and subsequently it reduced to 67.45% at 900°C suggestive of conversion to Cs_2O.

Strontium nitrate

The stoichiometric residual weight percent for conversion of $Sr(NO_3)_2$ to SrO_2 and SrO are 56.5 and 49 wt.% respectively. In our experiments during TGA the weight loss for $Sr(NO_3)_2$ started at 310°C. Initially the weight reduced to 75% at 445°C and subsequently the weight reduced to 40% at 700°C suggestive of full conversion to SrO. In batch calcinations studies for $Sr(NO_3)_2$ initially the weight reduced to 77% at 500°C and subsequently the weight reduced to 50% at 900°C suggestive of full conversion to SrO.

Cerium nitrate

The stoichiometric residual weight percent for conversion of $Ce(NO_3)_3.6\ H_2O$ to CeO_2, Ce_2O_3 and CeO are 39.6, 37.8 and 35.9% respectively. In our experiments during TGA the weight reduced to 40% at 160°C and no weight loss was observed on further heating. In batch calcinations studies the weight loss for $Ce(NO_3)_3.6\ H_2O$ was 49% at 400°C and subsequently the residual weight percent was 42.4 % at 500°C suggestive of full conversion to CeO_2.

Zirconium nitrate

The stoichiometric residual weight percent for conversion of $Zr(NO_3)_2.5H_2O$ to ZrO_2 is 40.36%. In our experiments the residual weight during TGA was 70% at 175°C and subsequently 40% at 320 °C suggestive of conversion to oxide. In batch calcinations studies initially the weight reduced to 49.4% at 400°C and subsequently to 42.7% at 500 °C suggestive of conversion to ZrO_2.

Chromium nitrate

The stoichiometric residual weight percent for conversion of $Cr(NO_3)_2.9H_2O$ to Cr_2O_3, CrO_3 and CrO are 38, 25 and 17% respectively. In our experiment the weight loss during TGA started immediately on heating and residual weight was only 7 % at 280°C. In batch calcinations studies also the weight loss started immediately on heating and residual weight was 18.4% at 500 °C suggestive of conversion to Cr_2O_3, and on further heating no weight loss was observed.

Barium nitrate

The stoichiometric residual weight percent for conversion of $Ba(NO_3)_2$ to BaO_2 and BaO are 64.7 and 58.67% respectively. In batch calcinations studies the weight loss for $Ba(NO_3)_2$ started at 600°C. Initially the weight reduced to 64.4% at 720°C and subsequently to 57.7% at 800°C suggestive of full conversion to BaO.

Calcium nitrate

The stoichiometric residual weight percent for conversion of $Ca(NO_3)_2.4H_2O$ to $Ca(NO_3)_2$ & CaO are 69.5 and 23.7% respectively. In batch calcinations studies the weight loss for $Ca(NO_3)_2$ started at 400°C. Initially the weight reduced to 62.3 % at 700°C and subsequently to 23.2% at 900°C suggestive of full conversion to CaO.

Cobalt nitrate

The theoretical residual weight percent for conversion of $Co(NO_3)_2.6H_2O$ to Co_2O_3 is 28.5%. In batch calcinations studies the weight loss for $Co(NO_3)_2.6H_2O$ was 28.5% at 400°C suggestive of full conversion to Co_2O_3.

Uranyl nitrate

The stoichiometric residual weight percent for conversion of $UO_2(NO_3)_2.6H_2O$ to UO_3 is 56.8 % and U_3O_8 is 55.73 %. The stoichiometric residual weight percent for conversion of anhydrous $UO_2(NO_3)_2$ to UO_3 and U_3O_8 are 72.39 %. In our experiments solution of uranyl nitrate was taken which was dried at 200°C. The TGA analysis of this salt showed that the residual weight percent was 72% at 300°C and 68% at 600°C suggestive of formation of UO_3 and its conversion to U_3O_8. In batch calcinations studies the weight reduced to 71% at 400°C and 66% at 800 °C suggestive of complete conversion to U_3O_8. This suggests that uranyl nitrate gets converted to anhydrous form at 200°C.

Copper nitrate

The stoichiometric residual weight percent for conversion of $Cu(NO_3)_2.3H_2O$ to CuO is 33%. In batch calcinations studies the residual weight percent was 33% at 500°C suggestive of full conversion to CuO.

Nickel nitrate

The stoichiometric residual weight percent for conversion of $Ni(NO_3)_2.6H_2O$ to Ni_2O_3 and NiO are 56.89% and 25.69% respectively. In our TGA experiment the residual weight percent was 20% at 250°C suggestive of conversion to NiO. In batch calcinations studies the residual weight percent was 93.6% at 100°C suggestive of conversion to $Ni(NO_3)_2.2H_2O$.

Iron nitrate

The stoichiometric residual weight percent for conversion of ferric nitrate to Fe_2O_3 and FeO are 56.89% and 25.69 % respectively. In batch calcinations the residual weight was 75% at 100°C subsequently it reduced to 18% at 500°C suggestive of conversion to FeO.

The results of the experimental studies of the waste constituents are summarized in Table I.

Table I. Thermograms of Chemicals in HLLW during Calcination

Temperature range °C	Physiochemical process
25 to 150	Water evaporation, saturation of solutions and precipitation.
150 to 300	Drying of slurry, loss of absorbed and bound moisture.
300 to 500	Decomposition of nitrates of Ni, Ce, Cr, Zr, Co, Cu, Fe to oxides.
700 to 800	Conversion of nitrates of Cs, Sr, Ba, Ca, U to oxides.

TO CALCINE OR NOT TO CALCINE

While there can be some Waste Management scenarios not necessitating calcination, prior to vitrification (even in metallic melter or cold crucible). It is not prudent to jeopardize a development because this technology can open many more options in future.

"To calcine or not to calcine" can become a real management concern for specific situations, the scope of this work was to focus developing and demonstrating a new technology. In this work logical deliberation for development of an indigenous calciner technology is described.

Fluid bed and Rotary Calciners are mainly used for processing of high-level liquid waste [3]. A comparison of important design and operation parameters was made, is shown in Table II. Rotary Ball kiln Calciner has important merits; this was taken up for development in Indian context. The design, operation and successful process demonstration is descried in this paper.

Table II. Comparison of Calciners in Main Usage

Parameters	Fluidized bed calciner	Rotary Ball Kiln Calciner
Heating Surface Temp. ^{o}C	600-800	Up to 800 ^{o}C
Temp. (^{o}C) of calcination	500-600	500-700
Product Properties a) Average Size (micro meters) b) Bulk density (gm/cc) c) Porosity (%) d) Product type	 250 – 1200 0.5 – 3.0 44 - 76 Spherical Regular	 130 - 160 0.65 – 0.95 69 - 79 Fragmented Regular
Off- gas generation	Very High	Minimum
Limitations	Process optimization important	Moving Parts & high temperature mechanical seals
Merits:	Good heat transfer, No moving parts	Minimum off Gases
Inventory/Hold Up	Less Hold up	Moderate hold up
Mode of Heat Transfer.	Convection	Convection/ conduction
Mode of product transfer	Numeric Transport	Gravity Transport
Entrainment	Moderate Entrainment.	Minimum Entrainment
Carry over of radio nuclides	Low Decontamination Factors	High D.F.

DESIGN OF ROTARY BALL KILN CALCINER

A minimum of 300 mm diameter of rotary calciner is necessary to obtain sufficient impact of steel balls on the rotating cylinder. The inlet hood has provision for feeding and the outlet end has been provided positive displacement motorized rotary valve for the removal of the dry calcined powder. The rotary shell has provision for variation of slope up to 5 degree between the

inlet and outlet end. The shell consists of 3 separate portions -precalcination, calcination and post-calcination zones. The central calcination zone has resistance heaters for heating up to 1000 °C. The maximum sagging /deflection of the rotary calciner has been calculated as 0.21 mm and 0.34 mm at ambient temperature and 815°C. The equipment specifications have been selected such that all parts are amenable for remote replacement, disengagement, encapsulation, storage and disposal. An electric resistance type rectangular furnace has been used for heating the Calcination zone. The furnace is having outer double walled mild steel casing with air gap arrangement and duly lined with lightweight ceramic fiber block insulation to reduce the skin temperature below 50 deg .C.

The furnace bottom is lined with ceramic fiber block insulation. The furnace top had lift-able cover for ease of maintenance. The furnace has Kanthal AF coiled coil heating elements on two sides and bottom. The power to the heating elements is controlled through three-phase angle firing mode thyristor. The structure is fabricated from mild steel and provided with screw jack arrangement for changing the inclination of the furnace to a maximum of 5 degree and with minimum elevation of 600 mm from floor level.

Rotary Tube

The Rotary Tube is made out of 300 mm OD, 10 mm thick S.S. 310 Grade material and the same is consisting of three separate portions of length 600 mm, 1760 mm and 600 mm for precalcination, calcination and post calcination zones respectively flanged together with 12 mm thick insulating type Gasket. 5 Nos. Grid plates of 280 mm OD, 10 mm thick with 20 mm diameter perforation holes are provided, at equidistant in the 300 mm long precalcination zone. 3 Nos. grid plates have been provided in calcination zone. The tube is filled with 25 mm diameter steel balls between grid plates. Zones are isolated by perforated grid plate arrangement. Φ20, 40 triangular pitch and 18 X 30 peripheral slots are provided for free flow of powder and off-gas. The details are shown in Figure 2.

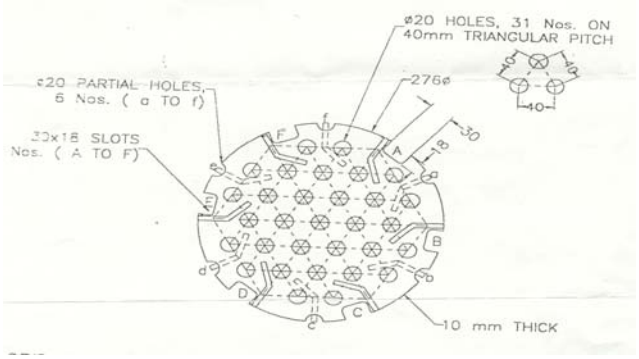

Fig 2. Design of central grid plates

- In the pre-calciner zone flat axial flights are used, while in the middle zone of the calciner for the semisolid slurry 135° lip flights are used and in the post calciner zone 90° lip flights are used.
- SS-310 balls Φ25 are provided in each zone for breaking the lumps, preventing deposition of scale, uniform mixing and provided extra heat transfer area as an extended surface.Variation

of slope: up to 5 degree by screw jack arrangement between the inlet and outlet end.Variation of speed: 1 to 12 rpm by thyristor power control.

HEATING FURNACE

- Box type resistance heating furnace, with ceramic fiber insulator.
- The furnace power rating is 24 KW, two equal (12 KW) at inlet and out let side.
- The furnace has Kanthal AF coiled heating elements.
- Heating elements on two sides and bottom.

Rotary Seals

- To avoid any leakage of hot gases in between the static parts and the rotating shell of the calciner, bearing housing with sealing arrangement is necessary. It is necessary to use mechanical seals for high temperature application. In order to test the process feasibility temperature silicon rubber seal were used.

- In order to reduce seal temperature seal cooling water is provided.

INSTRUMENTATION

The temperature measurement was done by 18 K-type thermocouples. Inside the calciner 6 numbers each at inlet & outlet end were used, at a depth of 500, 750, 1000 mm respectively. While outer shell of the Furnace had 6 thermocouples.

Temperature Control:

- ON-OFF controller controls inlet side of the furnace.
- Out let side of the furnace is controlled by PID controller with thyristor power controller.

Pressure Measurement

- Purge type pressure indicator with differential pressure transmitter is used to measure the pressure of both the sides.
- All I/O s' are remotely connected with Programmable Logic Controller (PLC) on line Data accusation system.
- Inter locking system is also provided. High Temperature inside the calciner automatically tripped the furnace.

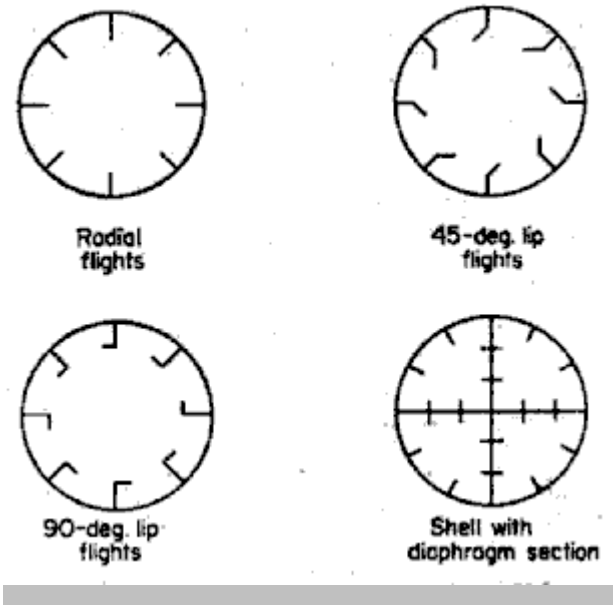

Fig. 3. Design of internal flights of Rotary Calciner

OPERATION OF ROTARY CALCINER

The Rotary Ball Kiln Calciner is a slowly rotating, slightly inclined tube, externally heated by means of electric resistance heating. The liquid is fed onto the moving bed of metal balls in a slowly rotating calciner. The balls crush the lumps formed during calcinations; also provide extended heat transfer area. A peristaltic type-metering pump does feeding after stabilization of inside temperature. By setting the calibration factor we can precisely control the flow rate, time can also set by automatic timer.

Experimental Operating conditions range:

- Feed flow rate –4 to 5 liter/hr
- Feed concentration- 300 gm/liter of strontium nitrate.
- Operating Temperature- 750-800 ^{o}C
- Slope- 1to2 ^{o}
- Rpm- 3 to 5
- Seal cooling water flow rate- 5-10 l.p.m.
- The temperatures were recorded at the depths of 500, 750 and 1000 mm both from inlet and outlet ends. The temperatures profiles were plotted along the longitudinal direction of the calciner.

EQUIPMENT SPECIFIC OPERATION PROCESS CONDITIONS

While the outer furnace attains steady temperature in about two hours – the temperature at 750mm and 500 mm depths stabilizes in 150/180 minutes. The temperatures were high in the middle portions of calciner. It was seen that the temperature difference between the outer shell and inner contents of Rotary tube were in the range of 100-150 ^{o}C. The heat transfer was more by convection than radiation.

CALCINED PRODUCT CHARACTERIZATION

- The powder was tested at 800 deg C had no weight loss, so complete calcination.
- Bulk density was 2.54 gm/cc.
- Particle size range 85-120 micron.
- The calcined product is hygroscopic, absorbs up to 10% moisture.

CONCLUSION

In a rotating shell the temperatures up to 700-800 degree C could be achieved with external heating. The dry strontium oxide calcined powder obtained by calcining strontium nitrate after heating at 800 degree C had no weight loss indicative of compete calcination. It had bulk density of 2.54 grams per c.c. The particle size was in the range of 85-120 micron. The calcined powder was hygroscopic as it absorbed up to 10 % moisture in 3-4 weeks.

The feasibility of Rotary Ball Kiln Calciner was tested and demonstrated. The dry calcined powder obtained by calcining has suitable characteristics for vitrification. In a rotating shell temperatures up to 800 degree C. could be obtained by external heating. Such system is feasible for calcination.

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