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A New Apparatus for Continuous Countercurrent Flow of Solids and Liquids

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ABSTRACT

A contactor was developed to provide true countercurrent, continuous flow of gel spheres and liquid in a moving bed. To provide smooth and controlled movement of solids, the key features consisted of a common cross section for the moving bed and a small fluidized bed, a jet to form a slurry at the bottom of the moving bed, and a controlled flow of part of this slurry to the fluidized bed. A completely continuous pilot plant for preparation of nuclear fuel by a gel-sphere process was operated with three of these moving-bed fluidized-bed contactors. Different control procedures and good countercurrent washing results were demonstrated.

Key Words. Moving bed; Liquid–solids contactor; Countercurrent flow; Particulate washing; Gel process

INTRODUCTION

Gel process for the preparation of oxide spheres commonly require washing to remove products and excess reactants present from the gelation reactions. An internal gelation process was applied to a number of metal oxides and mixtures (1). A different, external gelation using ammonia gas and solution has similar washing requirements (2). A review of gel processes (3) shows that four out of six types may require washing of the gel.

The mass-transfer requirements for washing gel spheres are very similar to those for stripping porous ion-exchange resins or adsorbents. When the gel processes are used to prepare nuclear reactor fuels, continuous countercurrent washing would have important advantages. Countercurrent washing is important for reducing the amounts of waste solutions. Contin-

uous washing allows useful capacities in equipment small enough for control of nuclear criticality by size limitations. Wet gel spheres can change or degrade with time, and continuous washing is desirable to ensure uniform and optimum characteristics.

The objective of this study was to select and demonstrate continuous, countercurrent contactors for gel spheres and process liquids. Because of the similarities to ion exchange, the literature on ion exchange is a logical source for concepts. While there are many patents that claim continuous ion exchange, Perry, Green, and Maloney (4) start a review by noting that there are no packed beds of truly continuous, countercurrent design in commercial operations. The contactors that have been described as continuous use intermittent flows, and some use mixed stages with countercurrent flow between stages.

In addition, Gilwood (5) notes that the large countercurrent ion-exchange installations are all processes in which the liquid flows alternate with periods for solids movement (without countercurrent liquid flow). He describes applications of the Asahi process with a bed packed by the upward flow of solution and cyclic interruptions in liquid flow to allow downward transfers of resin. Gilwood also provides descriptions of the contactors patented and described by Higgins and Chopra (6) and Himsley (7). The Higgins contactor uses valves to change the flow paths and give intermittent, alternating flows of resin and process solution. The Himsley contactor uses fluidized stages with intermittent bypassing of solution flow through a stage to allow the downflow of solids to the next stage. These intermittent or cyclic flow conditions may result in unacceptable attrition of the particulates. These conditions also result in much more mechanical complexity with respect to cyclic operation of many valves, and the use of more and larger flows requiring additional pumps and valves. The large and abrupt changes in flow rates can have undesirable effects.

DESCRIPTION OF REQUIREMENTS

Gel spheres are formed as porous solids, commonly of 50- to 5000-μm diameter, with the pores filled with solution. While some solutes can be vaporized or thermally decomposed, many must be washed out before the gel is dried. The gel sphere may be soft or sticky, and attrition, distortion, or clumping with losses of sphericity must be avoided. The chemical flow sheets for gel-sphere preparation of nuclear fuels had been developed and demonstrated using continuous formation of gel-spheres, but batchwise operations for aging, washing, and drying. Continuous countercurrent washing and aging were required for practical scale-up to a production capacity. A plant capacity of 0.1 MT/d of U + Pu would be equivalent

to 25 L/h of wet gel spheres. The design capacity selected for our equipment testing was one-fourth of this as a minimum, with the possibility of rates up to 0.1 MT/d.

The chemical flow sheet for the preparation of the gel spheres was approximately that reported by Haas et al. (8) for UO_3. The minimum times and wash volumes were determined by the requirements for leaching soluble reactants or products (NH_4NO_3, urea, hexamethylene-tetramine, and formaldehyde) from the gel. The washing should reduce these concentrations by a factor of 1000 from the initial concentrations, and this determines a minimum volume of wash. The minimum times are those for mass transfer in the gel when the wash volume flow rates are high to maintain low concentrations in the wash solution. Experimental results and calculations show that the washing of NH_4NO_3 agrees with diffusion coefficients of 0.66×10^{-5} cm^2/s within the gel sphere. The equilibrium distribution of NH_4NO_3 in volume concentration units is about 0.85 cm^3 of gel/cm^3 of wash. These results are reasonable since the gel primarily consists of water-filled pores and the theoretical diffusion coefficient for dilute NH_4NO_3 is $\sim 1.9 \times 10^{-5}$ cm^2/s.

The limiting requirements for sizing of the washing operation differ for large and small gel spheres. For the larger spheres (2000- to 5000-μm diameter), the limiting requirement is the holdup time to allow mass transfer inside the gel, which is about 1.5 hours for 4000 μm. For small spheres, the minimum wash volume becomes controlling as the superficial velocity must be limited to avoid fluidization or excessive pressure drops. Only a few theoretical stages of countercurrent washing are necessary to meet the washing requirements.

MOVING-BED FLUIDIZED-BED CONCEPT

The requirements for gel-sphere washing along with some experimental testing led to a new and successful concept. True countercurrent flow of gel spheres and wash solution requires liquid flow through a packed bed of particles without significant fluidization. The batch washing of gel spheres demonstrated that the spheres could be washed as a packed bed without damage, resuspended in wash solution, and transferred hydraulically. However, a controlled transfer of washed spheres from the bottom of a moving bed into a flowing stream is very difficult to accomplish. Arrangement to provide fluidization below the moving bed gave fluctuating discharges of solids from the moving bed and fluctuating rates of solids from the fluidized bed into a transfer line. The smoothest and best controlled transfers of gel spheres were into a transfer line at the top of a

fluidized bed with a large enough liquid flow to ensure a transfer as a dilute slurry of solids.

The above considerations led to the concept of combining a moving packed bed to give true countercurrent flows of gel spheres and solution with a fluidized bed to allow a controlled discharge of a dilute slurry. This concept still required a controlled movement of the solids from the bottom of the packed bed into the fluidized bed. A number of arrangements were tested experimentally and were not satisfactory. The first test units had single, uniform diameters for both beds (no changes in cross-section area) with a bottom jet flow to control a transfer from the moving bed to the fluidized bed.

Glass pipe test units were assembled from long radius elbows (a U configuration) with several different inlets for the jet liquid at the bottom midpoint. Others had 90° elbows at the bottom of the moving bed with horizontal or vertical jets in the elbow. Similar arrangements were assembled using bell reducers with the fluidized-bed diameter either the same or smaller than the moving bed. The bottom liquid inlets had several different diameters and included a variety of slotted and bent tubes at different locations. The operating difficulties (one or more for each arrangement) gave inadequate solids movement as follows:

1. The moving bed bridged at a bend or reduction so that there was no transfer of particles.
2. The flow toward the fluidized bed side channeled at the top of the horizontal section and then up the inner wall, leaving most of the particles stationary without adequate transfer of solids.
3. Large pockets of completely stationary particles were left in the bottoms of one or both columns.
4. Excessive slurry concentrations in the transfer line reduced the flow to zero or to a flow too small to discharge the particles at the required rate.
5. The rate of solids discharge cycled or fluctuated excessively, and these fluctuations would cause poor operation for the next process steps.

The combined moving-bed and fluidized-bed columns gave smooth controlled movements of solids when the following features were applied:

1. The fluidized bed was smaller in diameter than the moving bed, and the two were joined by 45°-long radius bends with a common vertical end plate at the bottom (Fig. 1). Each bed is uniform in diameter, and the opening between columns is a 45° cross section of the smaller column.

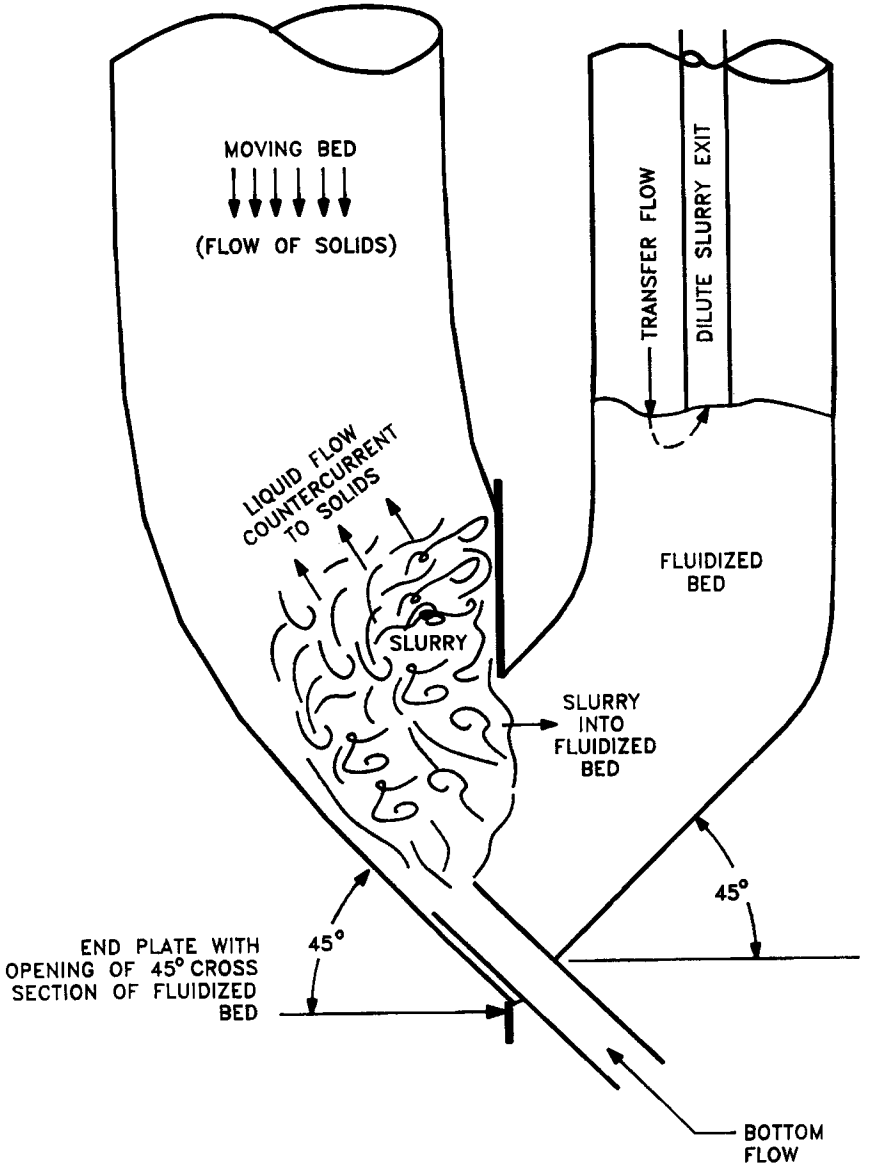

FIG. 1 Cross section of connecting configuration for moving bed fluidized-bed contactor.

2. A flow was jetted tangentially along the bottom wall of the moving bed without any change in cross section or sharp bend.
3. The transfer of solids from the moving bed to the fluidized bed was controlled by controlling the division of the bottom flow; that is, the amount of bottom flow that went to the fluidized bed side of the unit.
4. A liquid flow was added above the fluidized bed to ensure transfer of solids as a dilute slurry. The transfer flow was larger than the fluidization flow rate.

This combination of features was patented by Haas and Ryon (9).

APPARATUS

The critical configuration to join the moving and fluidized beds is a common vertical end plate with an inlet flow of liquid directed to slurry up the moving bed solids at the bottom end of the bed (Fig. 1). Each diameter remains uniform up to the common endplate, and long radius bends lead to the endplate. The opening between the columns is an angled cross-section (45° for 45° bends) of the smaller (fluidized) bed column. The bottom or control flow enters through a small tube and slurries an excess of moving bed solids (that is, more than the steady-state solids rate). Only part of this slurry flows into the fluidized bed and control of this fraction provides the control of the solid flow rate. The fluidized bed can be small in both diameter and height, and would then only contain a small fraction of the solids in the contactor.

The configuration shown in Fig. 1 was first tested for a continuous washing of gel spheres (Fig. 2). The test unit had a 7.6-cm-diameter moving bed and a 5.1-cm-diameter fluidized bed. This unit and other units of 10.1- to 7.6-cm-diameter and 7.6- to 2.5-cm-diameter combinations were used in a pilot plant. All combinations performed as intended, but a 10.2- to 5.1-cm-diameter combination would have been better than the 10.2- to 7.6-cm diameter combination that was used.

The equipment flow sheet for a continuous preparation of gel spheres on a pilot-plant scale included three moving-bed, fluidized-bed columns (Fig. 3). The aging column provided holdup time at controlled temperatures without any countercurrent mass-transfer requirements. The TCE wash column was a countercurrent wash to replace the gelation column organic with a volatile organic and did not involve mass transfer with the gel spheres. The three columns demonstrated different combinations of control procedures for the movement of solids. These differences will be discussed in a following section.

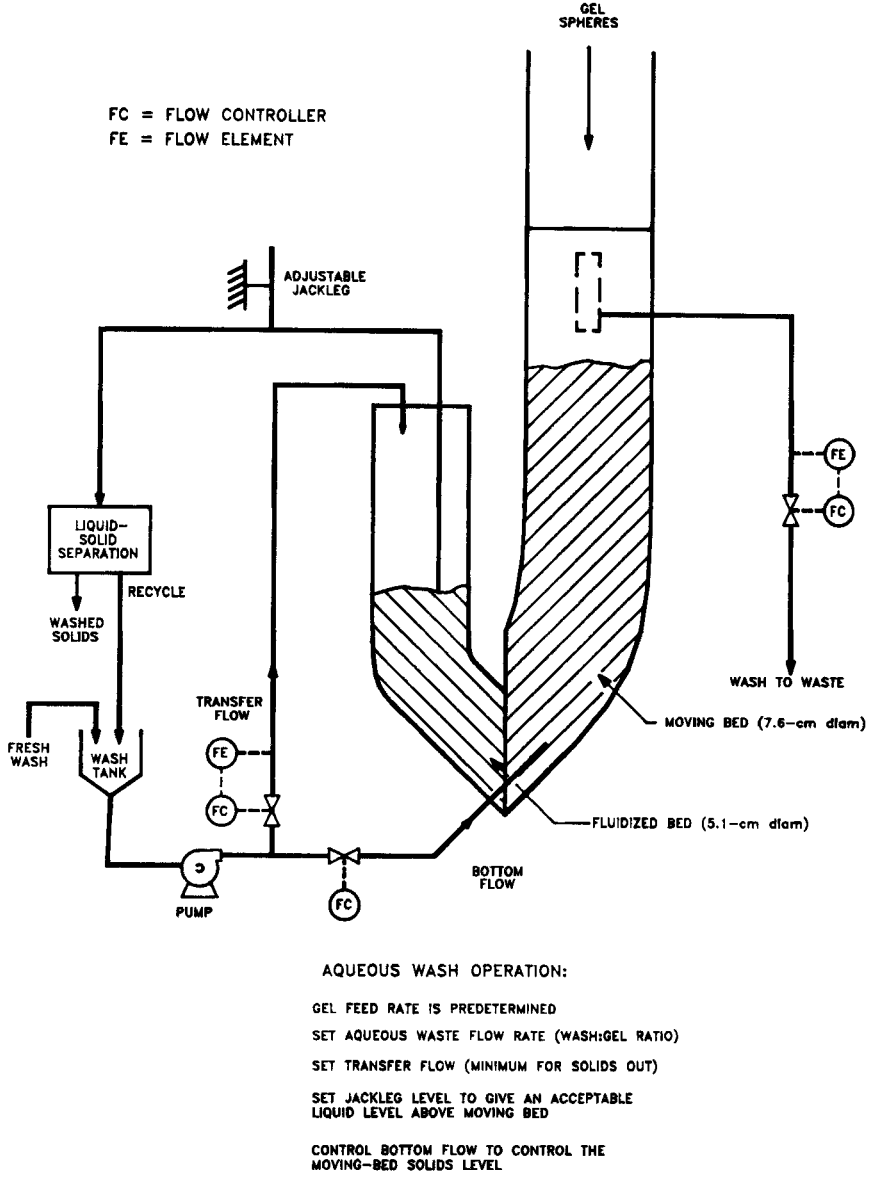

FIG. 2 Moving-bed fluidized-bed test unit for washing gel-spheres.

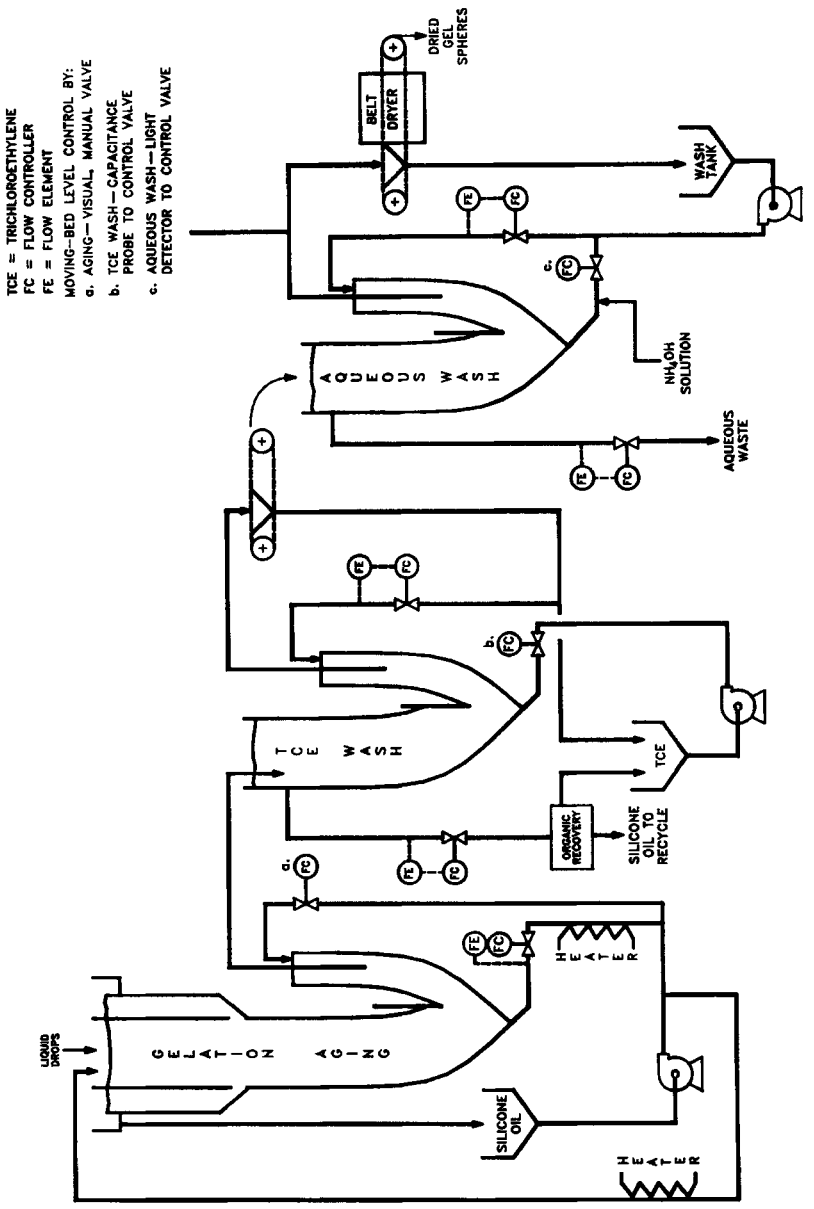

FIG. 3 A continuous gel-sphere pilot plant using three moving-bed fluidized-bed contactors.

CONTROL OF MOVING-BED FLOWS

An efficient, continuous countercurrent mass transfer in a moving bed requires the control of the two countercurrent flow rates—solids and liquid. Each control requires a measurement and a control action to maintain the desired value. For the gel-sphere processes discussed here, the flow rate of solids was predetermined by the selected production capacity. The size of each moving bed (volume and diameter) was then calculated using the known information on the minimum times and the maximum allowable superficial liquid velocities. The top levels of the beds were measured and controlled at the desired level using the appropriate liquid flow control (to be discussed later). The gel spheres settling into the aging (moving) bed displaced solids through the remainder of the system with constant, controlled inventories in each moving bed.

The liquid flow through the moving bed was controlled by metering the wash liquid flow out. When the tops of the moving bed columns are open to allow the feed of solids into the moving bed, any variations in liquid level yields corresponding changes in the liquid flow through the bed. The gel-sphere columns quickly reached steady-state liquid levels without difficulties from fluctuations. The gel-sphere liquid wash rates were estimated by the predetermined rate of solids flow and the liquid/solid ratio needed to meet washing requirements. A concentration measurement on the exit wash liquid (or the exit solids) could also be used to adjust the liquid wash rate to give a selected concentration.

The dilute slurry of solids was normally discharged through a jackleg (a vented weir). The jackleg level was adjusted as needed to give an acceptable liquid level above the moving bed. It is believed that this free discharge is much more dependable than use of a throttling control on a slurry flow. Since the exit flow of wash liquid and the solids inventory are controlled, all of the remaining flow must exit through the jackleg. The steady-state inlet flows will give a steady-state liquid level above the moving bed that gives the required steady-state flow from the jackleg. The jackleg can be raised to raise this liquid level or lowered to lower it. Flow of a dilute slurry allows smooth flow rates without fluctuations, while high exit slurry concentrations cause flow fluctuations that give fluctuating rates of solids transfer from the fluidized bed. The transfer flow to above the fluidized bed is set large enough to give good flow as a dilute slurry when the fluidizing flow is small.

The discharge of solids from the moving bed is a product of the slurry volume and the slurry concentration. The control of the solids occurs via control of the slurry volume by control of inlet liquid flows. The slurry concentration may depend on many variables including the effects of inlet

liquid flows, but the volume control provides adequate control of the solids flow rate. The inlet flows into the moving-bed column are the solids feed flow and the bottom liquid flow. The slurry flow by difference is the sum of these inlet flows minus the wash liquid out. Since the wash liquid flow rate out is controlled, changing the bottom flow in changes the slurry volume flow to the fluidized bed. Increasing the bottom flow produces a larger volume of slurry flow and decreasing the bottom flow yields a smaller volume of slurry flow. The liquid in this slurry is the liquid flow in the fluidized bed. The fluidized-bed diameters in this experiment were smaller than the moving-bed diameters so that fluidization could take place without use of an additional flow. Some other liquid–solid systems might require an additional inlet flow to provide good control of fluidization.

CONTINUOUS GEL-SPHERE PROCESSING AND WASHING RESULTS

Good operation of moving-bed fluidized-bed columns was demonstrated with gel spheres in an aqueous wash column (Fig. 2) and with three moving-bed fluidized-bed columns in a pilot plant (Fig. 3). The wash column test demonstrated good control of solid levels or solid flow rates for a wide range of solid and liquid rates. The pilot plant showed well-controlled solid transfer rates and steady-state operation for up to 1.4 kg/h throughput of UO_3 spheres (about 8 L/h) as a moving bed. The maximum test rates were limited by components of the gelation feed system, and the moving-bed fluidized-bed columns did not show any signs of overloading.

The aqueous wash column (Fig. 2) was tested by itself with a wide range of liquid and solid flow rates. The primary objective was to demonstrate good and independent control of the solids and wash liquid flow rates without detailed measurements of wash efficiency. The two liquid rates in and the wash rate out were measured and controlled. The gel spheres were added batchwise and the washed solids were collected batchwise. The top level of the moving bed was measured and the rate of change between feed additions was a measure of the solids flow rate. The glass pipe walls allowed visual observation of the bed levels and of particle movement. Operation with no transfer flow into the column caused cyclic flutuations of the solids loading in the discharge line, of the moving bed rate, and in the liquid level above the moving bed. With a good transfer flow, these fluctuations ceased. All aqueous flow rates up to fluidization and all solids flow rates up to overloading of the transfer flow (that is, excessive concentration of solids in this line) allowed controlled and uniform movement of solids in the moving bed. A controlled, uniform rate was possible for a

wide range of bed heights. The bottom flow entered through tubing in a slip fitting, and the length of tubing into the moving bed was a significant variable. With the tubing end flush with the wall, high bottom flows were needed to give good solid transfers. Insertions into the moving-bed cross section gave much higher solids transfer rates at the same liquid flow—probably because of higher slurry concentrations. This position can be varied to vary the fluidization flow and still maintain a desired solids transfer rate. Since the fluidization and transfer flow were separated from washed solids by a screen and returned to the wash supply tank, the net liquid flow to waste was that metered from above the moving bed. The few samples taken showed washing results that agreed with good plug flow of countercurrent solids and wash solution in the moving bed. At low flow rates, the washing exceeded the accuracy of analytical measurements. At high flow rates, the washing was controlled by diffusion in the gel spheres.

The aqueous wash column in the pilot plant provided the most complete test of the moving-bed fluidized-bed contactor. The overall results show good control of both the liquid and solid flows and good washing results. The top of the moving bed was detected by light transmission through the glass walls to a series of photoresistance cells (Fig. 4). This signal was used to increase or decrease the flow to the bottom of the moving bed. The exit waste flow was metered from above the moving bed. The volume of slurry from the moving bed to the fluidized bed increased or decreased with the bottom flow rate. Control of the top-bed interface was excellent after the control system was set to respond slowly to avoid cycling. The signal from the photoresistance cells showed some noise (Fig. 5), but the true bed height remained constant without any detectable variation by visual observation. The washed gel showed about 0.004 M nitrate as compared to about 2 M nitrate at gelation. The aqueous waste showed uranium concentration near the solubility limit for 0.3 N NH_4NO_3–0.2 N NH_4OH solution (that is, 20 to 60 ppm U). Attrition of the gel did not occur for the normal chemical flow-sheet conditions.

The organic wash column provided a demonstration of good control of liquid and solid flows and good removal of silicone oil without any mass transfer within the gel. The organic wash removed the nonvolatile silicone oil gelation liquid to discharge the spheres as a slurry in trichloroethylene. The trichloroethylene was easily and completely removed by air flow through a moving screen belt. Countercurrent flow of trichloroethylene through a packed bed of 7.6-cm i.d. and about 50-cm height (Fig. 6) gave complete removal of the silicone oil. The mixed organic wash waste was metered (pumped) from above the moving bed to a recovery system. A capacitance probe detected the top level of the moving bed of gel spheres and was used to vary the flow to the bottom of the moving bed. The volume

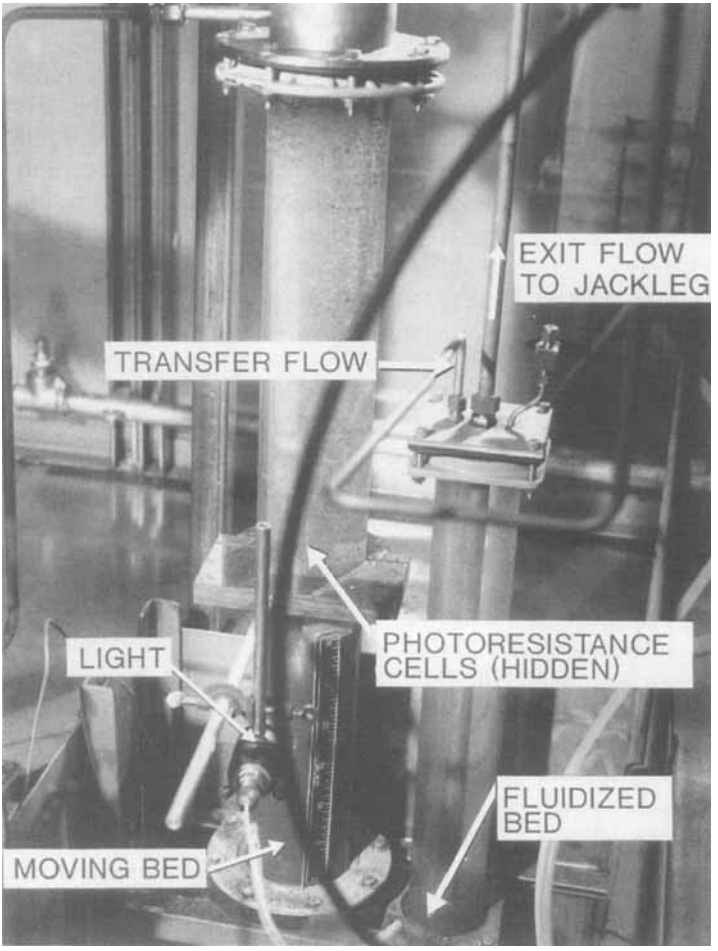

FIG. 4 A photograph of an aqueous wash column: 10.2-cm-diameter moving-bed and 7.6-cm-diameter fluidized-bed.

of slurry flowing into the moving bed increased or decreased with the bottom flow.

The aging column provided a plug flow of moving gel spheres at a controlled temperature to allow aging to give consistent and reproducible gel properties. The only need for a countercurrent liquid flow was to improve the uniformity of aging temperature. In the gelation column, a constant liquid level above the moving bed was important for good operation of the drop formation for the uranium solution feed. Therefore, a

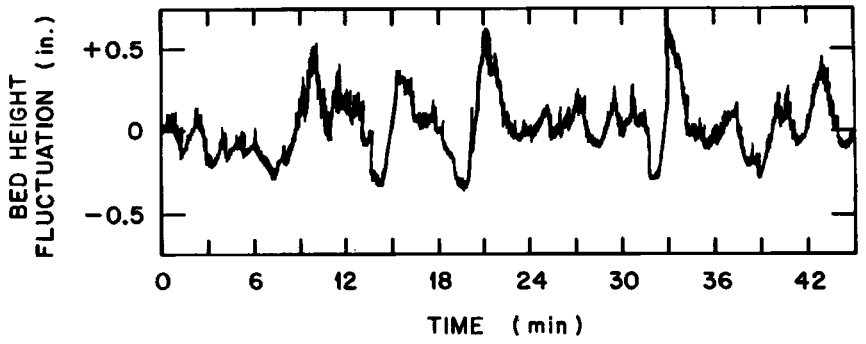

FIG. 5 The aqueous wash column bed height indicated by a photoresistance level detector.

weir overflow was used without control of the overflow rate. The jackleg (a vented weir) for the exit flow above the fluidized bed controls the flow of this slurry stream. The total of the inlet flows to the gelation and aging column minus the flow through the jackleg exits over the weir above the moving bed. A flow of hot organic provides a control of the gelation temperature. The flow through the jackleg is determined mainly by the difference in the two weir levels and varies little or none with variations in the flow to the bottom of the moving bed. Therefore, changes in the bottom flow do *not* give the control of solids flow rate (this is different from the other two columns). The flow of slurry into the fluidized bed (that is, the solids flow rate) in the aging column can be varied by varying:

1. The jackleg level, since lowering the jackleg increases the total flow and increases the amount of flow from the moving bed (at a constant transfer flow rate).
2. The transfer flow rate, since decreasing the transfer flow increases the flow from the moving bed, and increasing the transfer flow decreases the slurry flow from the moving bed.

Controlling a flow is more convenient than moving the jackleg. Therefore, the aging times were controlled by visual observation of the bed level and occasional manual adjustments of the transfer flow rate. The jackleg level was adjusted only for major changes in test conditions in order to adjust the division of exit flows between the weir and jackleg exists. The moving bed for aging was 7.6-cm-diameter and was most commonly 30- to 40-cm high. The viscous silicone oil did not allow enough flow through the moving bed to control the temperature in the bare glass pipe, and surface heaters were used to make up the heat losses.

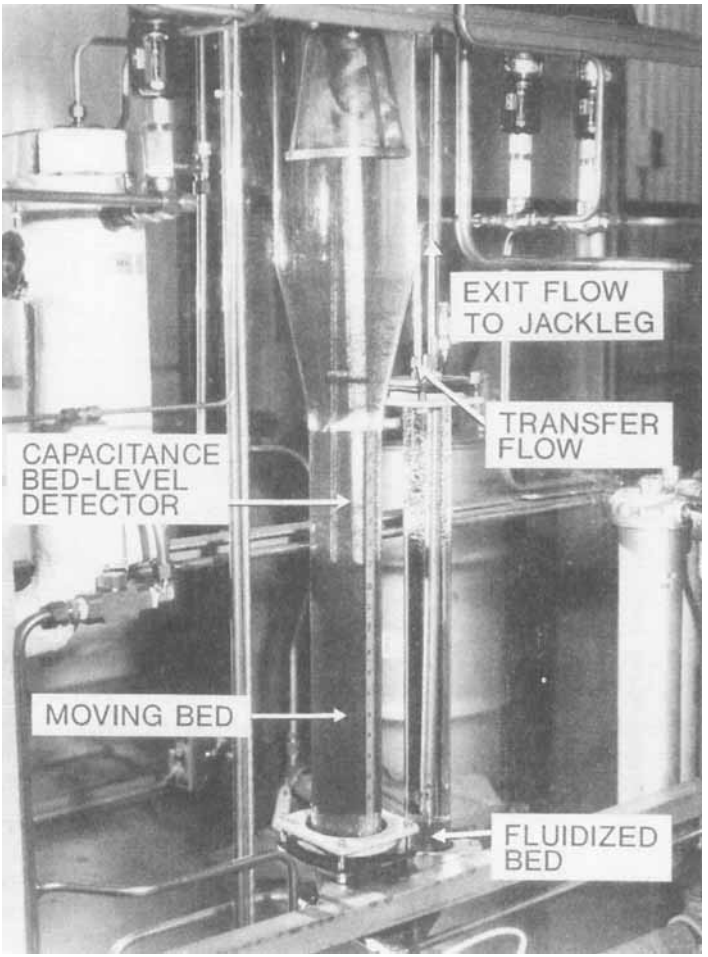

FIG. 6 A photograph of an organic wash column: 7.6-cm-diameter moving-bed and 5.1-cm-diameter fluidized-bed.

Several types of level detectors were tested for indications of the moving-bed levels and each had limitations. The light detectors gave good control of the aqueous wash contactor, but they require a transparent column. Capacitance element probes were effective for gel spheres in trichloroethylene or silicone oil, but could not detect gel spheres in aqueous wash solution. A sonic detector gave a good indication of a settled interface, but was disturbed by falling or suspended particulates. The natural radia-

tion of process materials is variable and would complicate the use of a radiation source and detector for particular levels.

The moving beds were easily and smoothly filled with gel spheres at the start of test runs and emptied after the gelation was stopped. At the end of tests, the flows were simply set manually to continue at the same rates without regard to the bed-level indications. Only small adjustments in these flows were necessary to give almost complete removal of spheres from the contactors. At startup, the flows were set to give the normal moving-bed liquid flow, no flow of slurry to the fluidized bed, and little or no fluidization flow. The control procedure for solids flow was started after the moving-bed column had filled to near the normal level.

RESULTS AND CONCLUSIONS

Good continuous, countercurrent operation of a moving bed of solids and liquids was achieved by an apparatus that joined the moving bed with a small fluidized bed. Flow of solids from the top of fluidized beds with an additional flow to give a dilute slurry results in a smooth and trouble-free transfer. After testing a number of unsuccessful concepts, controlled transfers of particulates from the moving bed to the fluidized bed were achieved by a combination of:

1. A moving bed of uniform diameter and a fluidized bed of smaller uniform diameter joined by 45°-long radius bends to a common vertical end plate.
2. A flow was jetted tangentially along the bottom wall of the moving bed to form a slurry of particulates in liquid.
3. The transfer of solids was controlled by controlling the amount of the above slurry that moved into the fluidized bed column.
4. A transfer flow was added above the fluidized bed to dilute the flow from the top of the bed to a dilute slurry.

A column with a 7.6-cm-i.d. moving bed and a 5.1-cm-i.d. fluidized bed was tested with continuous countercurrent flow of UO_3 gel spheres and aqueous ammonia wash solution. Uniform and well-controlled rates of solid movement for a wide range of liquid/solid ratios were demonstrated. The liquid flow for the fluidization and for the transfer as a dilute slurry were separated from the solids and returned to the wash supply tank. The net flow of liquid to the waste is the flow through the moving bed.

A continuous pilot plant for preparation of nuclear fuels by a gel-sphere process was operated with three moving bed fluidized-bed contactors. Steady solids transfer rates and satisfactory operation was demonstrated for 1.4 kg/h throughput of UO_3 spheres, or about 8 L/h as a moving bed.

ACKNOWLEDGMENT

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