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THE APPLIED DEVELOPMENT OF THE PULSE COLUMN

by

J. P. Duckworth

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ISOICHEM INC.

Richland, Washington

THE APPLIED DEVELOPMENT OF THE PULSE COLUMN

Beside me is a model of a pulse column like those used in the Isochem Inc., Chemical Separations Plant at Hanford, Washington. Its purpose is to serve as a mixer or contactor to carry out the liquid-liquid separation process necessary to separate uranium, plutonium and neptunium from fission products and from each other. I will not go into details about the process at this time since it is well defined*, but it is used throughout the world in the field of reactor fuel reprocessing and is known as the Purex process. Purex stands for plutonium-uranium recovery by extraction. This process employs nitric acid as a fuel dissolution and aqueous salting agent and TBP (tributyl phosphate) diluted in a kerosene base solvent as a complexing organic liquid. By contacting various ratios of these two immiscible liquids with controlled amounts of nitric acid, the heavy metal ions - uranium, plutonium and neptunium - can be transferred from the aqueous liquid or phase to the organic phase and back again achieving the desired effect of separating these materials from the waste fission products. The fission products are formed in the reactors as a by-product from the production of plutonium and neptunium. The Purex process is based on fundamental equilibrium and distribution data developed originally at the Oak Ridge National Laboratories about 1948.

Though the process is basic, the application varies throughout the world, and a trick of the trade, so to speak, is to carry out the process as simply and as efficiently as possible. This is very important since the radioactivity

* Reactor Handbook, 2nd Edition, Volume II, Fuel Reprocessing, S. M. Stoller and R. B. Richards, Interscience Publishers, Inc., New York, 1961.

associated with irradiated fuels requires special materials of construction for all equipment in contact with the solutions and sizeable expenditures for buildings with the necessary shielding and means of handling the fuels and equipment. This was the primary reason the pulse column was selected at Hanford as the contactor for the Purex process.

The operating principal of the pulse column is the same as that used in a butterchurn. Only instead of the paddles with the holes going up and down, the liquid is moved up and down past a rigid paddle with holes called a cartridge. Both methods achieved the same result, that is, the mixing or dispersing of two immiscible liquids. The application of this principal to the chemical plants at Hanford represents a prime example of integration of the chemist, chemical engineer and mechanical engineer. Its development and applications has been a team effort with representatives from each of these fields working side by side. The chemist developed and defined the flowsheet in the laboratory, the chemical engineer applied the flowsheet by defining equipment and process needs, and the mechanical engineer defined the strength of material, types of energy required, and the mechanisms. For example, chemists found that by mixing uranyl nitrate and nitric acid in aqueous solutions with TBP in kerosene, the uranium would transfer from the aqueous to the organic TBP phase. However, in the absence of nitric acid, it goes back into the aqueous phase. The chemical engineer found that by using a pulse column as a mixer, the transfer could be achieved in the shortest amount of time and in equipment requiring the least amount of space. The mechanical engineer found that by using a mechanical piston on a hydraulic leg, the amount of flexibility and reliability necessary for remote operation could be obtained. Of course

other disciplines were also consulted and integrated in this type of application, such as instrument engineers, physicists, electrical engineers and civil and architectural engineers. But in the latter case, they supplied the services or support features to the primary process or equipment.

All this serves as an introduction to the actual development of the pulse column. As you can see, it is principally a pipe with enlargements on both ends. The inside contains a cartridge, which is the "heart" of the column, consisting of a uniform array of rigidly held plates pierced with holes called sieve plates. A hydraulic leg extends from the bottom of the column to a mechanically operated piston. The concept is simple. A heavy immiscible liquid is fed into the top or middle of the column and a lighter immiscible liquid is pumped into the bottom. The heavy liquid should fall and the lighter liquid rise, and thus the two liquids contact each other and any chemical transfer possible can take place. This works but is not very efficient since the amount of transfer is proportional to the surface area of the two liquids in contact. In packed columns, the packing serves to slow up and disperse the liquids and thereby increase the surface area of contact. The pulse column does this by making bubbles or droplets. The plates used usually have holes sized so that the surface tension of the heavier liquid will not allow it to fall, or flow through the plates by gravity. Therefore, when a pulsing action is applied, the lighter phase is pushed up through the holes and the heavier liquid is pulled down through the holes. This, of course, forms droplets of both phases which increases the surface area of contact of the two liquids. The more droplets of each phase, the greater the surface area and the more efficient the contact. However, as you know, if you make the droplets too fine you will

homogenize the liquids and then you have defeated the purpose. Also, after a droplet is formed and has reached equilibrium with the surrounding liquids, no further useful transfer is accomplished. Therefore, the droplets have to be collected or coalesced and the liquid re-dispersed into droplets. So for maximum efficiency, we want to make and break bubbles as fast as we can without homogenizing the liquids. This is where the applied development has paid off at Hanford.

Initial pilot plant data on pulse columns up to 6-inches in diameter proved that the same separation efficiency could be obtained with a pulse column which was only half the height of a comparable packed column. However, when the development data was scaled up to columns 24-inches in diameter, it was found that channeling or the non-uniform dispersion of liquids in the column, decreased the efficiency to below acceptable limits and almost caused the abandonment of this type of contactor. Many concepts were tried to overcome channeling, such as spray rings, sectionalizing the columns, impellers, etc., until a young engineer came up with the idea of the louver plate. This is a plate with four slanted openings, like half opened trap doors located on the radius of the plate. These louvers caused the pulsed liquids to swirl on each stroke and thus circulate the liquids horizontally to the normal flow which breaks up any tendency to channel. By spacing louver plates systematically in the cartridge of a pulse column, columns as large as 36-inches in diameter and 40 feet in height are successfully used without problems of channeling.

Another applied development was the plastic plate. Because of the extreme radiation conditions of the process solutions and the chemical conditions of

the process, stainless steel is used for most of the equipment, including the column, cartridge and pulsers. Of the two liquids used; aqueous nitric acid and TBP in kerosene, the water preferentially wets the stainless steel; therefore, in columns with stainless steel cartridge, the water will coalesce faster than the organic, thus making the column essentially filled with the aqueous solution, while the organic is dispersed into droplets. We call this type of operation, aqueous continuous. As a result, the interface between the two phases, forms at the top of the column where there is minimum energy and the organic has time to coalesce. This is very good in some columns, but in an extraction column where we want to transfer the product from the aqueous to the organic phase and take the product off the top in the lighter organic phase while the waste drops out the bottom in the heavier aqueous phase, the "crud" (solids and impurities), that form at the interface, breaks off and follows the product, thus nullifying some of the benefits achieved during the extraction. To eliminate this problem, plastic plates were developed of fluorothene and linear polyethylene, which are wetted by the organic liquids rather than the aqueous and thus allows the column to be operated organic continuous with the aqueous phase dispersed and the interface of the two liquids at the bottom of the column. The "crud" then leaves with the waste. This improvement increased the efficiency of operation but it was found that the service life of the plastic plates exposed to high radiation fields was too short and their replacement too costly, especially in the initial extraction column, so that their use was curtailed. This limited the application of the columns until another engineer came up with the idea of a nozzle plate. This plate is made of stainless steel and has holes like a regular sieve plate but around each hole an indentation is made. When these plates are inserted

in a column with the nozzles pointing down, they tend to trap a thin layer of the lighter organic liquid under the plate between the indentations which acts as an organic coating and forms a coalescing surface. This favors the organic phase and allows the column to operate with the organic phase continuous. The development of the nozzle plate has made the service ability and reliability of the pulse column competitive with almost any type of contactor.

We also used stainless steel plates coated with linear polyethylene and cartridges with Raschig rings packed between the plates. Another important development in cartridge design has been the variation of spacing between the plates. Initially, a uniform spacing was employed, but now, by varying the spacing, types of plates, free area and hole sizes of the plates, additional efficiency and capacity has been achieved.

In the model, the bottom half of the cartridge is constructed of nozzle plates, while the top, which is not exposed to as much radiation, is a combination of plastic and sieved plates. There are louver plates in each section. The top portion of the cartridge has been named a "zebra" cartridge, because of the striped or banded type of operation. The purpose of this arrangement, once seen, is elementary. If we want to make and break bubbles and have conditions where coalescence of one phase is favored over the other, by continually changing the phases while you are making the bubbles, you can assist in the coalescence and dispersion of the two phases. In the model, the heavier aqueous phase is green and the lighter organic phase is clear. By changing the plate surface to favor coalescence, we change the continuous phase and thus have a striped - zebra - appearance.

There are many combinations of cartridges that can be used and recently a cartridge was developed called a "sandwich" cartridge which is constructed of 3/4-inch thick plastic plates sandwiched between two stainless steel sieve plates and these, in turn, are spaced between sections of nozzle plates. This type cartridge, used in stripping - the transferring of product from the organic to the aqueous phase - not only increased the efficiency of the column but also increased the capacity. There are many other combinations used and, in fact, the door is just opening on cartridge design since now that the pulse column has been proven as a reliable, efficient contactor, new applications in other types of industry are being explored.

Also at Hanford, the cartridges were originally built into the columns, and to change a cartridge, the entire column had to be replaced. Now all the new columns are being designed with removable cartridges which can be exchanged or replaced. As a result, the Purex Plant, which was originally designed for the processing of uranium and plutonium only, is now capable of operating on four different flowsheets. The number of products separated has been increased from 2 to 6; the capacity of the plant has been increased about four times the original design capacity; and efficiency has been improved by reducing the required number of cycles to achieve the necessary separation and decontamination from 3 to 2. This has lowered the operating cost appreciably and reduced the losses to waste by almost one-half. All of this has been done in less than ten years. Much more can be done but it will require continual applied development.

I stress applied development because I want to make it clear that most of the improvements made to date have not been from the theoretical or advanced research approach. They have come as the result of trial and error and

application of basic engineering principles. Process and development engineers, working as teams in the field with the process and equipment, have solved the problems as they have developed. A prime example of this is the interface control system for the bottom interface extraction columns.

The interface detection device for top interface columns consists of air purged dip tubes similar to air bubbles or fish bowls which indicates the interface by measuring the pressure required to cause air to flow through two separate tubes located at different fixed depths in the liquid. As the specific gravity of the liquid changes, the pressure changes and the location of the interface is indicated. When this device was tried at the bottom of the column, the energy from the pulser caused so much pressure variation that the pressure signals from the dip tubes were completely masked and, therefore, could not be used. A conductivity probe was next tried, using the principle that the acid aqueous phase was more conductive than the organic phase. This worked in the pilot plant tests but, in practice, the layer of "crud" which forms at the interface occluded so much aqueous in the organic phase that no sharp differentiation of the interface could be detected. A capacitance probe was also tried but this also proved unsatisfactory since the "crud" filled the small space between the two capacitors causing unreliable readings. Finally the problem was solved by using the principle of a toilet bowl float in conjunction with that of a electronic rotometer. By fastening a float onto the soft iron core of a rotometer and allowing the core to move up and down inside the magnetic field of a wire coil, we have been able to develop a control system which will allow the detection of an interface to within one-eighth of an inch at the bottom of a column operating with 1-inch pulse

amplitudes at a frequency of a hundred cycles per minute. There are many more examples, such as this, that I could cite but I believe that this demonstrates my definition of applied development. This area of engineering work is just as important as basic research in the advancement of any technology. And in the chemical processing field, there is a lot of room for improvement.

Regarding the design and operation of a pulse column, there are many variables to be considered. I have mentioned such variables as material of construction, types of plates, plate spacings and hole sizes which relate to the cartridge of a pulse column. In addition to these, there are physical variables such as specific gravity of the solutions, viscosities, temperatures and surface tensions which need to be considered. Also, the chemical variables, like salting agent concentrations, organic complexant concentrations, product concentration, and chemical stability to oxidation and reductions are basic factors which have to be considered. For the pulsers, the frequency, amplitude of the stroke, shape of the wave formed by the stroke, and the speed of the stroke are some important variables for the efficient operation of the column. Other variables associated with the operation of a pulse column under equilibrium conditions include volume velocity, or total flow rate, flow ratios of the aqueous and to organic liquids, AF product, or the energy input measured by the amplitude times the frequency of the pulser, distribution coefficients or the equilibrium concentration between two phases, and HTU, the height of a transfer unit, or HETS, the height equivalent to a theoretical stage. These and other variables, such as radiation stability of the chemicals and surface finish of the plate materials must be considered in the application of a pulse column. The importance of a specific variable depends on the intended service of the

individual column. Usually, the variables are evaluated for every new process. So you can see that the range of variables has not been completely defined and until they are, the advancement of the pulse column will remain as much an art or applied development as it is a technology.

Right now, at the Purex Plant at Hanford, we are testing a new diluent. The diluent is the carrier for the viscous high density tributylphosphate complexant. Initially a narrow range kerosene cut was used. Later a more stable petroleum fraction consisting of naphthalenes was used. This was replaced with a synthetic iso-paraffin diluent. Now we are testing an economical normal paraffin diluent. We have reason to believe that this will give us better column stability, increased capacity, and improved radiation stability to chemical reactions. But it will require a year or so before the specific benefits can be defined.

Today we have columns for extraction, stripping or back extraction, scrubbing, washing and partitioning or chemical oxidation-reduction reactions. Also, pulse column principles have been applied to ion exchange systems where the resin is used as the solvent or organic complexant. We have compound columns, such as the model, where the bottom half is the extraction section and the top is the scrub section. More complex columns have been designed and built. One has seven input streams, at various points, and two or three output streams. Such a column, we feel, is just another step in the advancement of the pulse column which shows there is broader application and utilization for them. The model is approximately 1-inch to 1-foot scale and it includes some other mechanical features used in association with the pulse column. The pulser is

operated by a variable speed motor coupled to an off centered or cam drive which activates the external yoke. The yoke is fastened to a piston. The cylinder holding the piston is connected to the column through a large pipe called a pulse leg. The amplitude of the stroke on the piston is fixed by the cam size. The necessary flexibility is achieved by varying the speed of the motor and, therefore, the frequency of the pulser. The pulser, though mechanical, has proven to be extremely reliable with the major problems resulting from leaks developing at connecting flanges. The pulser represents a development effort which started with the use of a bellows and then progressed to air pistons and finally mechanical drives. The piston is sealed with graphite rings and the mechanical parts are lubricated by a built-in lubrication system.

A deep well turbine pump is operating the cylindrical tank. This model is a five-stage pump. We use these pumps to move liquids at rates varying from 1/2 to 100 gallons per minute against hydraulic heads of from 10 and 150 feet. The pumps vary from 3 to 15 feet in length and we obtain the necessary flow and pressure requirements by varying the number and locations of the stages. Recently, an idea was applied to the pump to solve a need for mixing a tank. Holes were drilled in the side of the bottom stage which allows jets of liquid to flow out across the bottom of the vessel. The turbulence achieved from this action is sufficient to uniformly mix two incoming solutions while continuously pumping from the tank.

The small pump on the model is a magnetically driven centrifugal pump and is used to eliminate the problem of leakage through mechanical bearings.

Chemical processing and more specifically the application of the pulse column to chemical processing as a field or area of engineering interest has a lot of room for growth and new ideas. Development work is in progress on automating simple columns. But thus far, the advancement of applied development has progressed faster than theory and is not waiting. As we increase the complexity of the pulse column, we increase the complexity of the operation and much work remains on instrumentation for better control on deentrainers and separators, on flow control and measuring devices, on new materials of construction and less expensive means of pulsing. So you see, even though the pulse columns is a remarkable example of applied development, it has by no means reached the peak and there is still need for a great deal of improvement, waiting for young men and women like you to develop and apply to this engineering tool.

THIS IS A PHOTO
OF THE WORKING
MODEL WHICH
WILL BE USED
WITH ISO-SA-6

A SPEECH ON
PULSE COLUMNS
TO SERVE AS A
RECRUITING AID

W.P. McGuire
2-28-66