Continuous Liquid-Liquid Extraction Via an Improved Centrifugal Contactor

(Special Shared Content with CINC)

Summary

An improved annular centrifugal contactor design is being commercially employed in numerous liquid-liquid extraction applications. It is mechanically driven by a directly coupled motor at relatively low rotor speeds. The combination of interchangeable heavy phase weirs and variable rotor drive makes this centrifuge applicable to a wide range of processes. Single stage efficiencies of 90% or higher are typical for chemical systems with rapid kinetics. Mixing and disengaging times range from 10 to 30 seconds each, dependent on the feed rate to the unit and the unit size. Efficient two phase mixing is achieved in the annulus between the spinning rotor and fixed housing. For versatility, a low mix sleeve can also be used to process shear sensitive liquids, often encountered in washing applications.

Annular centrifugal contactors with rotor diameters of 5 to 51 centimeters which range in throughput from 2 to 750 liters per minute are now readily available. The criteria used to select the proper size and operating parameters needed will be discussed. In addition, convenient methods of using this technology to convert batch to continuous processing will be given. Advantages in yield improvement and waste minimization will be discussed, and process equipment footprint will be given. Finally, some field examples which describe the versatility of this liquid-liquid centrifugal contactor will be presented.

Introduction

General Centrifuge

Clarification of process streams has been one of the niches in the process arena carved by liquid-liquid centrifuges, especially whenever emulsions or liquids close in density have been involved (Davies et. al., 1972). Difficulties that often arise in separation of immiscible liquids include: poor or slow phase separation, emulsion or rag layer formation, and poor process control in batch systems. Centrifuges accelerate separation processes by enhancing the specific gravity differences. Liquid-liquid dispersions requiring hours to separate at 1G will proceed much faster at 100 to 1000 G, with greatly improved efficiency and outflow quality. The efficiency of the physical separation of two phases can be several percent higher using centrifuges versus decanting from tanks.

Contactors as Extractors and Washers

Liquid-liquid centrifuges are valuable separation devices because of their small size and the rapid, yet efficient operation. However, they become even more valuable when employed as liquid-liquid contactors. The ability of a centrifuge to thoroughly mix two phases in the annular zone prior to separation in the rotor broadens its scope. Good mixing is very important to ensure optimal mass transfer and to minimize solvent or water usage. Chemical processes requiring extraction and washing (or neutralization) as well as separation can be performed in one step utilizing liquid-liquid centrifugal contactors. Better process control, low retained fluid volume during processing, and reduced plant space usage are realized when using these devices in place of traditional tanks, mixer settlers, and extraction columns.

Annular Centrifugal Contactor

History

Annular centrifugal contactor design and development has been pursued by various Department of Energy labs for more than 30 years. It has been employed in solvent extraction processes for metals valuable to the nuclear industry. Commercialization of this technology began in 1990 when a patent was granted for continuous separation of hydrocarbons from water (Meikrantz, 1990). In the past four years the centrifuge design has been further improved and scaled up to flow rates of several hundred gallons per minute (Meikrantz et. al., 1997). In addition, a low mixing sleeve which enhances the washing and separation of shear sensitive liquids has been developed (Meikrantz et. al., 1996).

The annular centrifugal contactor possesses many unique design features that distinguish it from other centrifuges on the market today. It has an upright design in which the vertical rotor pumps, thereby feeding itself. A self-pumping rotor maintains separation equilibrium during intermittent feeding because a constant liquid volume is maintained in the rotor. Liquid-liquid separators that require direct feeding to the rotor are not as capable of handling processes where interruptions in flow often occur.

Another advantage of a self-pumping rotor is the method by which a process stream is fed to the centrifuge. Because the liquid need only be fed to the annulus, any low pressure pump or feed supply can be used. Other types of liquid-liquid contactors require high pressure to feed liquid to the rotor. This poses a significant barrier to potential users processing liquids with specific gravity values of 0.8 or less. The only pumps capable of generating these high pressures are regenerative turbine pumps which are expensive, noisy, and high maintenance.

Commercial Annular Centrifugal Contactor

Principle of Operation

The annular centrifugal contactor operates as both separator and contactor which makes it a valuable tool in numerous types of processes. It's unique design provides mixing and separation in a single, compact unit. Figure 1 shows a cutaway view of the centrifuge housing and rotor and details the significant design features including the liquid flowpath.

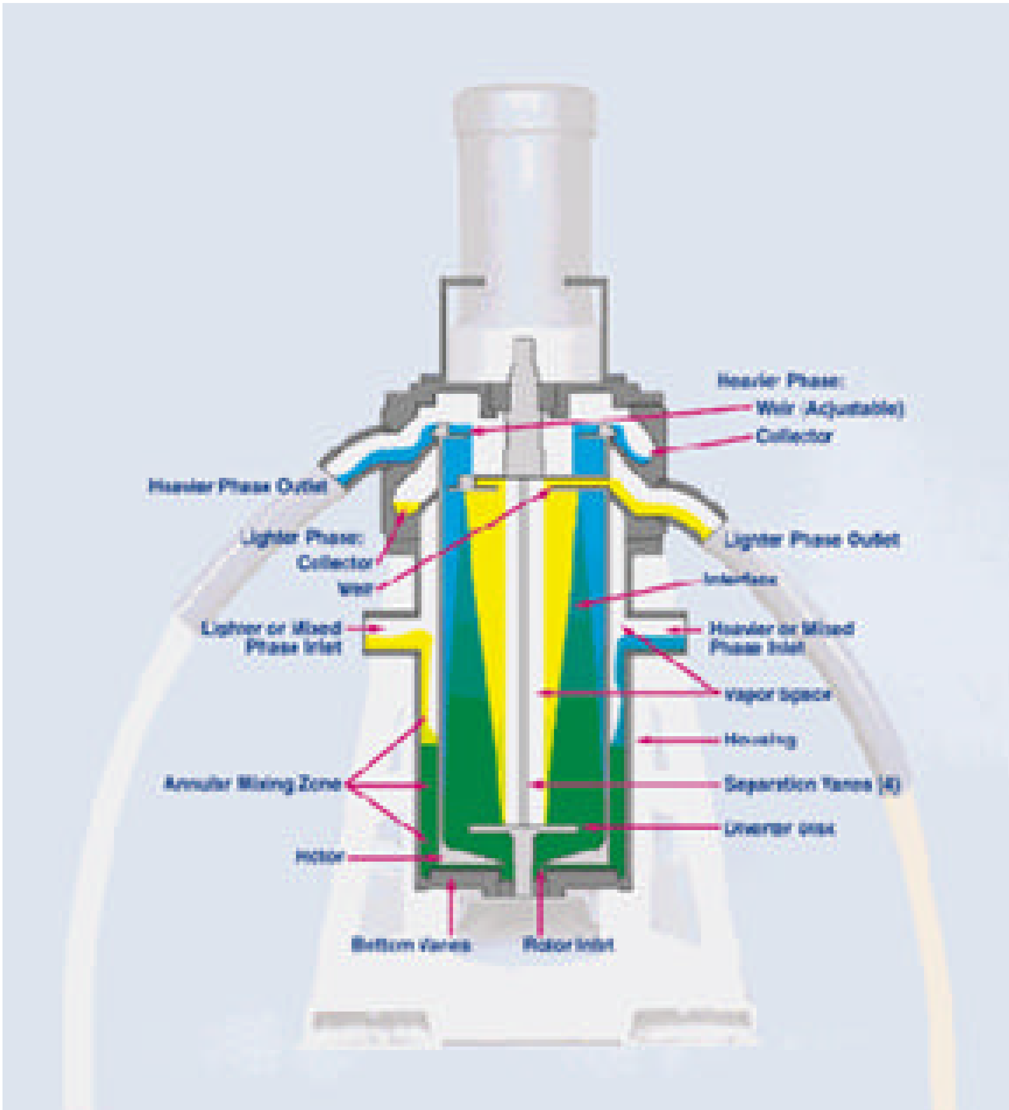


Figure 1: Cutaway View of Centrifugal Housing

Two immiscible liquids of different densities are fed to the separate inlets and are rapidly mixed in the annular space between the spinning rotor and stationary housing. Please note that the areas above the liquid levels are vapor space. The mixed phases are directed toward the center of the rotor bottom by radial vanes in the housing base. As the liquids enter the central opening of the rotor, they are accelerated toward the wall. This self pumping rotor is divided into four vertical chambers which are dynamically balanced by the pumped liquids. The mixed phases are rapidly accelerated to rotor speed once trapped in a quadrant, and separation begins as the liquids are displaced upward by continued pumping. The separating zone extends from the diverter disk to the lighter phase weir, which provides a transit time for the liquid-liquid interface to form and sharpen. The interface should be positioned half way between the lighter phase weir and the heavier phase underflow at the top of the separating zone. This is done by selecting the proper heavy phase weir ring and then adjusting the rotor speed to fine tune position if necessary. Optimum performance is thus achieved despite changes in flow rate or liquid ratios because the interface position can shift a significant distance without loss of separation efficiency. Because the interface is free to adjust in position, it is important to keep the liquid discharges unrestricted in terms of liquid and vapor flow and pressure. Equilibration of pressure between the centrifuge housing, discharge pipes, and receiver tanks ensures trouble free operation over a wide range of process conditions.

Low Mix Option

In process situations where only a two phase separation is being performed or shear sensitive fluids are employed, excess mixing in the annulus needs to be minimized. To accomplish this, a low mixing sleeve can be used, which is a cylinder slightly larger than the rotor. It is permanently attached to the bottom of the housing. By shrouding the rotor, liquids entering the annulus do not come in contact with a high shear surface, but instead enter a primarily static environment. The radial vanes in the bottom of the housing are still present so that the liquid flow path to the rotor is unchanged. Liquid-liquid shear is minimized yet the pumping action of the rotor is not adversely affected. Mixing of the two phases occurs as the liquids are accelerated to rotor speed and pumped. This action is vigorous enough to provide an efficient washing step in many shear sensitive processes.

Take Apart Rotor/CGMP Design

Many process streams include small amounts of solids and particulates that build up on the internal surfaces of the rotor even though filtration is used. Eventually these solids will impact the separation efficiency of the centrifuge. Many pharmaceutical and chemical industry applications require thorough cleaning between batches to ensure product purity. Cleaning of the annular centrifugal contactor can be accomplished in two ways. The two liters per minute laboratory scale model has a rotor which can be completely disassembled for cleaning and inspection of the internals. The rotor can be removed from the housing by the operator with simple tools. Removal of the vane package and heavy phase weir exposes all internal surfaces for cleaning. The frequency of cleaning is dependent on the percentage of particulates in the process stream. These features are also available on the next larger model which processes up to 20 liters per minute. Both units utilize a rotor suspended from the upper bearing housing to enhance disassembly and simplify the design. Good manufacturing practice requirements for these centrifuges are readily addressed by the use of castings to eliminate welds or crevices and by the ability to inspect all wetted areas.

Clean in Place Rotor

Large, high volume annular centrifugal contactors require a rotor bottom tail shaft to add stability. These rotors are suspended between an upper and lower bearing and, coupled with the size and weight, makes frequent disassembly for cleaning impractical. Therefore a clean-in-place (CIP) rotor (Figure 2) has been developed.

Clean-In-Place Rotor

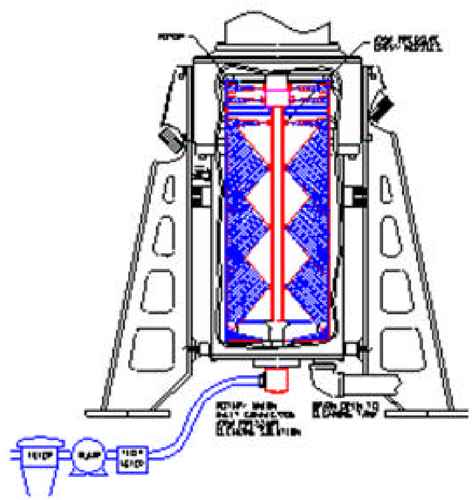


Figure 2: CIP Arrangement

A hollow through-shaft is employed which starts below the bottom plate of the housing and extends into the upper rotor assembly. It is equipped with a series of high pressure spray nozzles for each quadrant. These nozzles provide complete coverage of the internal wall of the rotor, the aqueous underflow, and the upper rotor assembly. A rotary union that is permanently attached to the tail shaft provides the inlet for the desired cleaning solution and allows the cleaning process to be fully automated. The process steps for cleaning are quite simple. Product feed to the centrifuge is halted and the rotor is stopped, which drains the holdup volume into the annulus. Next, draining the process liquid from the centrifuge exposes all the internal rotor surfaces to the cleaning solution spray. Cleaning solution is then pumped to the centrifuge via the rotary union until the unit is clean. After sufficient cleaning, the process is reversed and the centrifuge is put back in service. The total operation is performed in minutes requiring no disassembly of the unit or connection and disconnection of supply lines. When multiple units are set up in parallel to handle a continuous process, sequential cleaning can be used to avoid flow interruptions. The extra centrifuge is the off-line unit and the cleaning process simply shifts from one to the next while the remaining units continue operation.

Processing Principles

The annular centrifugal contactors are low rpm, moderate gravity enhancing (100-1000 G) machines, and can therefore be powered by a direct drive, variable speed motor. The effectiveness of a centrifugal separation can be easily described as proportional to the product of the force exerted in multiples of gravity (G) and the residence time in seconds or G-seconds. Achieving a particular G-seconds value in a liquid-liquid centrifuge can be obtained in two ways: increasing the multiples of gravity or increasing the residence time. Creating higher G force values for a specific rotor diameter is a function of rpm only, which is limited by direct drive motor capabilities. Figure 3 shows a plot of RPM versus G-force for various rotor diameters. Normally 4000 to 12,000 G-seconds of force is adequate to efficiently separate two immiscible liquids in most processes. For separations where the specific gravity differences are slight, G-seconds as high as 50,000 can be obtained by merely slowing the feed rate to the contactor or by upgrading to the next larger size unit.

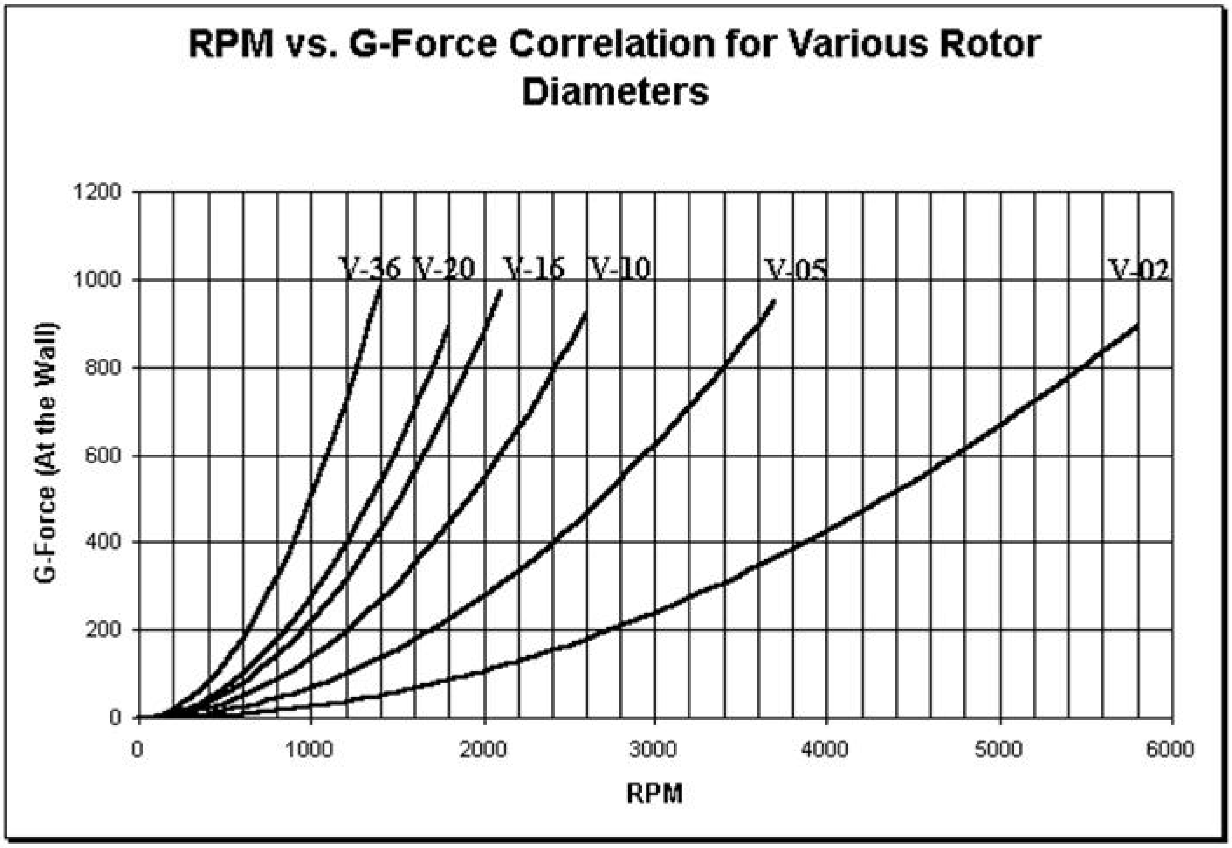


Figure 3: Plot for Various Root Diameters

Figure 4 is a plot showing the residence time versus flowrate for a 12.7 cm. diameter rotor. As a general rule, the residence time increases proportionately with rotor diameter. Therefore, a 25.4 cm. diameter rotor will provide twice the residence time of a 12.7 cm. diameter rotor at maximum operating flow.

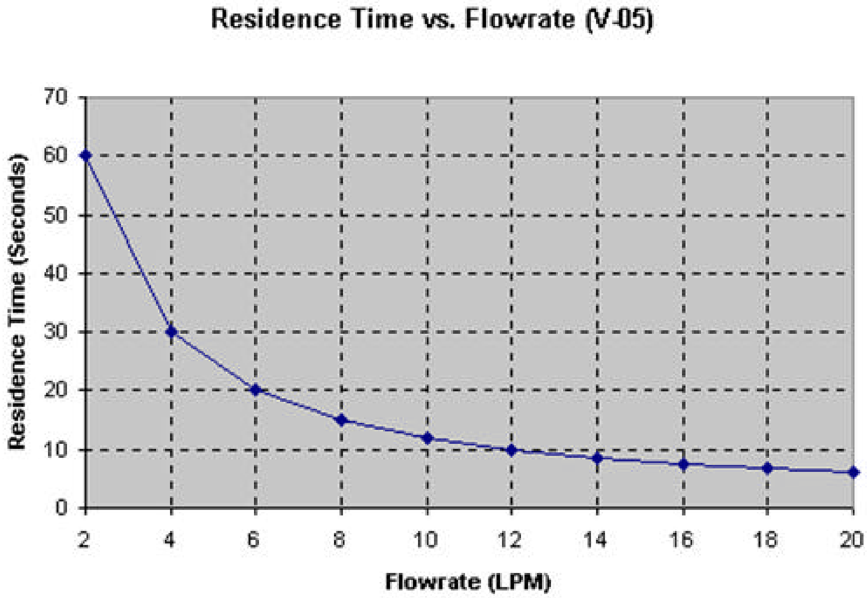


Figure 4: Residence Time/Flowrate Plot for a 12.7 cm Diameter Rotor

Extraction processes are based upon selective distribution. Transfer of a specie between phases must make allowance for intimate contacting and separation of the phases (Oliver, 1966). For extraction and washing purposes the ability of the contactor to efficiently mix two phases is vital. It is also important that over-mixing does not occur to avoid emulsification which results in poor separation. Several variables for mixing control are available to the operator of the annular centrifugal contactor. Varying of the rotor speed changes the linear speed of the rotor surface thus effecting the mixing shear. Table 1 shows a comparison of the linear mixing rates at 200 G for the various rotor sizes. Flow rate to the contactor also plays a role in the degree of mixing. A high flow rate results in a higher annulus level providing more mixing between the phases and the spinning rotor. These variables can be used to process shear sensitive fluids while addressing cases where high energy mixing is required for optimum mass transfer. The kinetics of certain extraction systems may also dictate that more annular (mixing) residence time is necessary for maximum efficiency. Additional stages may be required to meet these requirements.

Table 1: Rotor Linear Mixing Rate

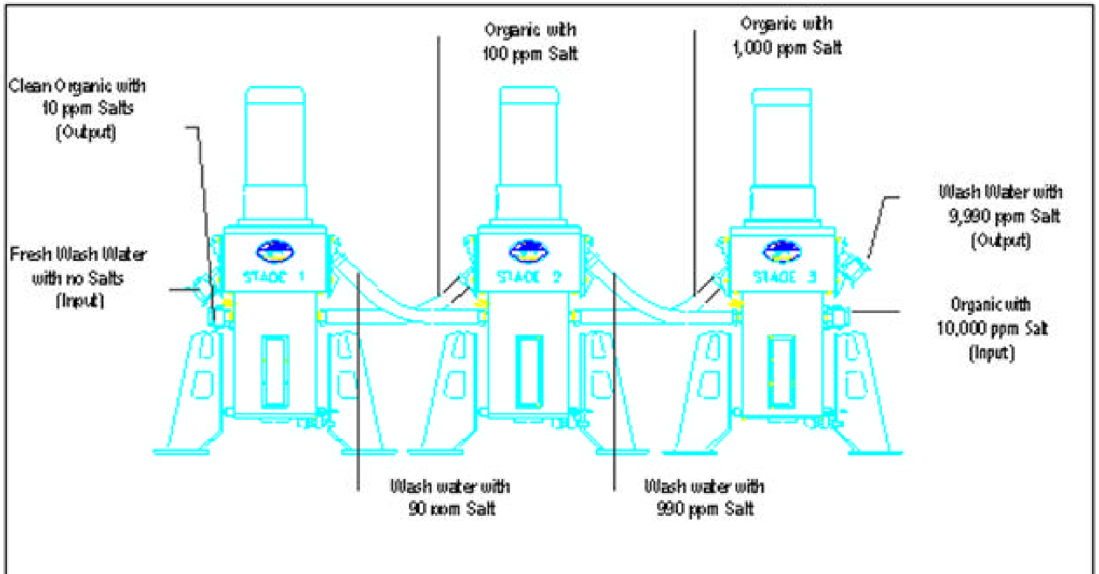
Diameter (cm)	***Mixing Rate (m/s)***
5.0	7.01
12.7	11.60
25.4	16.50
40.6	20.1
50.8	21.6

Conversely a low flow rate does not generate a high annulus level because the liquid is drawn into the rotor almost immediately. Such a situation does not afford much mixing due to minimal annulus residence time and rotor contact. This reduced mixing parameter can also be better attained through the use of the low mixing sleeve. With the surface of the rotor shrouded, the liquids are no longer subjected to the linear mixing shear, and the only annular mixing is due to contact from fluid flow into the annulus. As mentioned previously, some mixing of the two phases occurs as the liquids are accelerated to rotor speed. In washing procedures where kinetics are not an issue, this phase contact is often sufficient. This approach should be taken when employing shear sensitive fluids for washing or extraction. The ability to vary the separating and mixing parameters makes the annular centrifugal contactor more versatile than many of its counterparts.

Sometimes chemical processes require more than just the separation of two liquids of a process stream. The annular contactor has two inlet ports for introduction of solvents and washing solutions, making it an excellent device for extraction applications. Efficient two phase mixing is achieved in the annulus between the spinning rotor and the fixed housing. Mixing and disengaging times range from 10 to 30 seconds each, depending on the feed rate to the unit and unit size. Single stage efficiencies of 90% or higher are typical for solvent extraction systems with rapid kinetics. The advantages of using centrifugal contactors versus columns or mixer-settlers for extraction, washing, and neutralization are numerous. Reagent volumes required for a specific process are much less than comparably scaled reactions performed in tanks or other vessels. Rapid mixing and separation can enhance product recovery and quality. This is especially true in processes where product degradation occurs under separation conditions due to prolonged contact with either pH extreme solutions or reagents that continue to react with the product. Achieved separations are better than when normal decant methods are used; and this saves product, time, and minimizes waste.

Multistage processing

Continuous separation, washing, and extraction processes often require many steps or stages to achieve desired product quality or required extraction efficiencies. Centrifugal contactors can be readily interconnected to allow multistage processes (Figure 5). This is a three stage counter current washing process in which an organic solvent contaminated with 10,000 ppm salts is washed with fresh water. We assume 90% efficiency at each stage.



Three Stage Counter-Current Wash Scheme

Figure 5: Multistage Processing

Because the discharge ports are at a higher elevation than the inlets, pumps are not required to feed from stage to stage. For example, a multistage counter-current wash process would only require two feed pumps, one for each liquid phase. In this case, the barren wash water in stage 1 contacts the cleanest organic in order to remove the remaining small amount of salts, acting as a polishing step. In stage 3, semi-loaded wash water contacts the pregnant organic feed, thereby maximizing the efficiency of the wash. Receiver tanks collect the washed organic product and the salted waste water exiting from stages 1 and 3, respectively. This feature eliminates numerous pumps, tanks, and level controls. Such a system occupies only a fraction of the operating floor space of a corresponding batch process.

A further example of a multistage process is given in Figure 6. In this case, six inter-connected stages provide a continuous metal extraction, scrub, and strip process. No intermediate pumps or tanks are required for the continuous phase as it traverses the complete separation. A 90% efficiency is assumed and a 1:1 aqueous to organic ratio is used to quantify the interstage metal concentrations in the 3 stage extraction part of this process. Counter current flow in both the extraction and strip stages is employed to gain maximum efficiency while minimizing reagent usage.

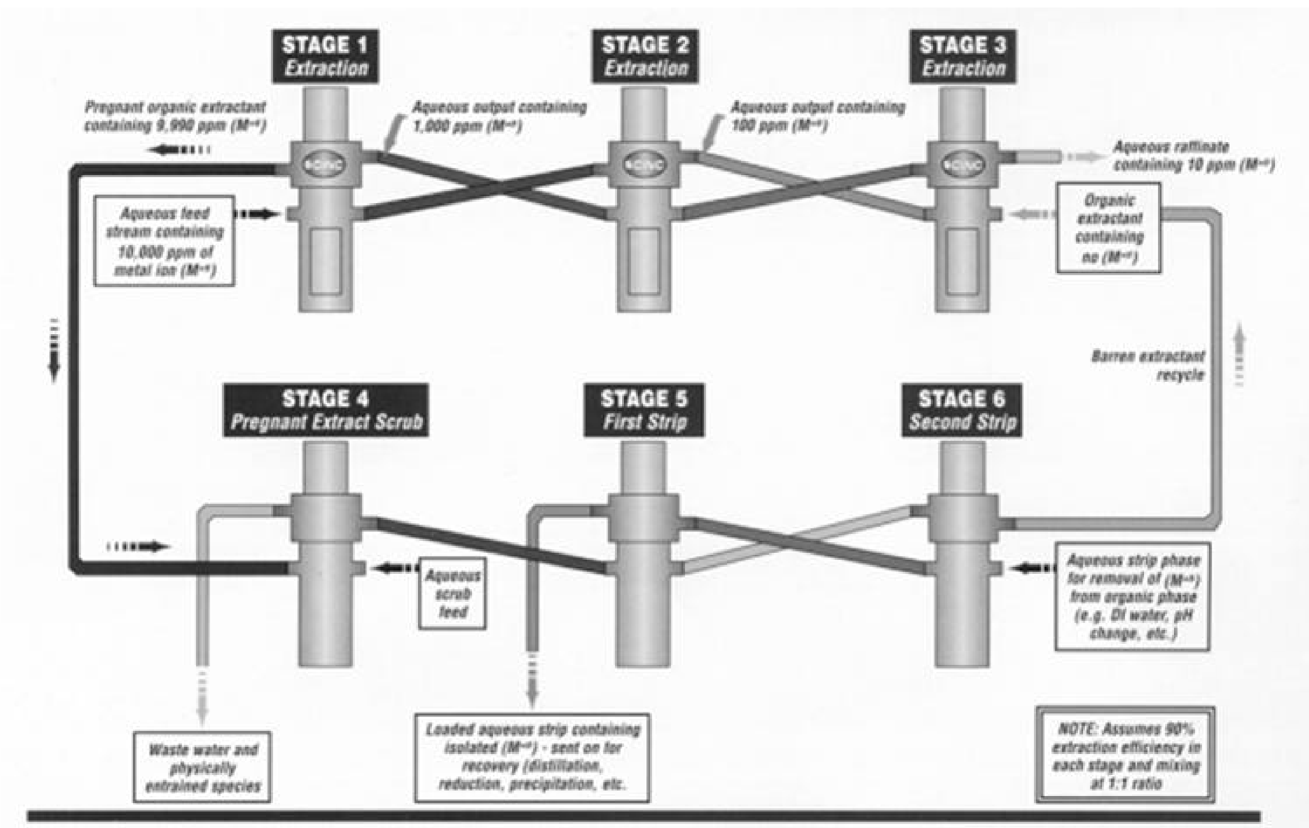


Figure 6: Six Stage Continuous Metal Extraction

Field Applications

Although employed by the Department of Energy for decades, this technology has only recently become commercially available. Therefore, a broad base of industry experience is lacking at this time. However, as more than 65 annular centrifugal contactors have been sold during the past two years, more data and experience is forthcoming. Numerous studies, especially with the laboratory scaled unit, are in progress in such industries as mining, metals recovery and purification, and chemical and pharmaceutical production. Conversion of separation, washing, and extraction processes from batch to continuous is rapidly gaining importance due to higher efficiency goals and increased waste management costs.

A good example of a commercial installation took place in April, 1997 at Great Lakes Chemical at El Dorado, Arkansas. An annular centrifuge contactor was installed as the first step in converting a batch process to a continuous operation following the reaction sequence. It replaces a 4,000 gallon decant tank by efficiently separating the brominated polymer product from the aqueous waste at the rate of 45 liters per minute. The increase in efficiency thus gained has been measured as a 3% improvement in product recovery, which represents 136,000 kilograms of brominated polymer worth $400,000 per year.

The contactor has been operating continuously without problems while being fed in batch mode from the multiple production reactors. In addition, off normal, emulsified product batches which previously were processed off-line are no longer a concern. The enhanced separation power of the annular centrifugal contactor operating at 300 times gravity processes all product rapidly and efficiently.

A second Hastelloy C-276 contactor has been purchased for the next process step, hydrochloric washing of the polymer phase. When installed, this unit will remove unreacted amine from the product and will enhance the recycling of this starting material. Coupling the second unit to the first will be simple and will make the process even more cost effective to operate.

Conclusions

Annular centrifugal contactor designs of this type are a significant improvement over traditional methods of liquid-liquid processing. Increased productivity from continuous or simultaneous multiple step processes as well as improved finished product quality from better process control is realized. Rapid and efficient separation prevents significant product loss at the liquid-liquid interface and from unwanted reactions resulting from prolonged contact times. Multistage separations and extractions utilizing annular centrifugal contactors not only minimize water and liquid reagent usage but also occupy a minimum of floor space compared to the alternatives. Low maintenance due to moderate operating speeds and ease of cleaning means downtime is reduced thereby maintaining process efficiency.

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 By: David Meikrantz, Scott Meikrantz, and Mitch George, Guest Authors, meikdh@inel.gov