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THE STACKED-CLONE CONTACTOR: A HIGH-PERFORMANCE HYDROCLONE SOLVENT EXTRACTION DEVICE

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ABSTRACT

The stacked-clone contactor, which is a high performance liquid-liquid solvent extraction device, has been developed to the point where a stainless steel prototype using integral pumps and capable of application to radio-chemical processing has been designed and fabricated. The principle of operation, using individually driven hydraulic cyclones coupled by the induced underflow effect, has been shown to be applicable to many different solvent extraction systems including 100% tributylphosphate vs 3 M sodium nitrate, methyl isobutyl ketone vs dilute acetic acid and 120 cp mineral oil vs dilute nitric acid. Extraction stage efficiencies are generally about 70% for the less viscous systems but drop to about 30% for the very high viscosity systems. Throughputs which reduce the contact time to less than 3 sec per physical stage have been realized.

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THE STACKED-CLONE CONTACTOR: A HIGH-PERFORMANCE

HYDROCLONE SOLVENT EXTRACTION DEVICE

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The stacked-clone contactor is a high performance solvent extraction device with a unique principle of operation. The word clone is a contraction of hydroclone, or hydraulic cyclone, the component which, along with its associated pump, comprises the stage of the contactor. The application of the hydroclone to solvent extraction was suggested by the discovery of the induced underflow effect at the Oak Ridge National Laboratory while studying hydroclones for cleanup of the fluid fuel of the aqueous homogeneous reactor. The hydrodynamic behavior of a hydroclone is characterized by rotational flow. The conservation of angular momentum as the fluid progresses from a tangential inlet port to a centrally located vortex finder (see Fig. 1) accelerates the fluid giving rise to both a high centrifugal field and a high shear field within the cavity. In addition to this primary flow, there are strong secondary boundary flows. Due to the local collapse of the centrifugal field by drag along the wall surfaces, flow progresses down the wall and, in fact, out of the underflow port. When the underflow discharges into a closed chamber this boundary flow is balanced by a return flow up the vortex. Within the cavity of the hydroclone, then, we find a high shear field for mixing, a high centrifugal field for separating phases, and an inherent countercurrent flow which comprise all of the necessities for a good solvent extraction contactor. The development of the stacked-clone contactor was concerned primarily with exploiting these effects and finding a suitable way of coupling hydroclones to form a cascade.

A small chamber was provided between the overflow of one stage and the underflow of the next. The pump circulation circuit for a stage includes the underflow chamber, a plenum connected by a radial gap to this chamber, the pump, the feed port of the hydroclone, the vortex finder, and finally the underflow chamber again. Note in Fig. 2 that the countercurrent flow is not effected by the pumps, which simply drive the stages, but is inherently present in the cavity of the clone. The shape of the hydroclone was modified from the conventional conical design to a more stubby cylindrical design in order to obtain higher induced underflow rates and to reduce the holdup volume per stage. One end of the cascade terminates with the overflow from the hydroclone discharging into a gravity settling device where the organic or light phase disengages and is drawn off as product. The heavy or aqueous phase is not clarified but is recirculated through the top stage pump with from 10 to 25% by volume organic phase, see Fig. 3. The other end of the cascade is terminated with a set of three or more polishing stages beyond the point at which the organic or light phase is fed to the cascade. These stages serve to remove the entrained light phase from the heavy phase effluent. The total

cascade then operates like any countercurrent contacting device where the net rates at any section are determined by the feed and effluent rates. Pictures of the experimental unit studied at the Oak Ridge National Laboratory are shown in Figs. 4 and 5 where it is apparent that the cascade is operated in a horizontal position. Since the centrifugal field in these devices is in the order of 1000 g, gravity has little influence on performance. Figure 4 shows the polishing end of the cascade where the clarification of the aqueous effluent stream can be seen. The hydroclone cavity has a diameter of 1.5 in. at the top, with the cylindrical section having a 0.5-in.-diam. A stage is 5.5 in. long. The recirculation rate to drive the stage is about 20 liters/min which yields a total countercurrent throughput of 3 to 4 liters/min. Pumps work with a pressure of about 15 psig. The original experimental stacked-clone contactor was built with demountable separate components (Fig. 6). This flexibility made it possible to study the effect of various design configurations. Among the most important configuration variables were the shape of the clone cavity and the underflow chamber. The first experimental model, Mark I (Fig. 7), used a conventional hydroclone design with an underflow chamber separated from the pump suction plenum by a small gap. This design proved quite workable but had the disadvantage of a small size and low capacity. There was some fear of the ports plugging. The unit might have been scaled geometrically to a larger size, however, the behavior of liquid-liquid systems in hydroclones does not scale predictably and the capacity of the hydroclone increases as the square of the dimension while the volume increases as the cube. For these reasons it was decided to explore modifications of the standard design. The next experimental model was a drastic step away from the standard design in that the clone body underflow port was extended into a cylindrical section. The nominal diameter of the clone was increased from 0.5 to 1.5 in. while the length was maintained approximately the same. The underflow chamber became part of the bottom of the clone with a simple tangential take off eliminating the separate plenum, and the vortex finder was reduced to a simple orifice. This device performed very poorly. Rounding of the shoulders did not significantly improve it. It was not until the pump suction plenum was again isolated from the rotational field inside the clone by a flow restricting gap that the performance of the device again looked promising. This is shown in Mark III-C and V. Mark IV, Mark VI and Mark VIII were studies of the effect of the underflow chamber. In Mark X, the underflow chamber was again flattened and made similar to the underflow chamber in Mark I. Mark XI, which is the latest and most successful design, is different from Mark X only in that the flow path from the vortex finder into the underflow chamber has been smoothed.

These studies were conducted on an experimental device such as shown in Fig. 8 where only four extraction stages were used and the pumps attached to the clones by plastic tubing. With this unit studies were made of the effect of the length of the clone cavity, the vortex finder length and diameter, the feed channel size, the underflow chamber volume, the size of the gap connecting the underflow chamber to the pump plenum chamber, and general studies on accessories and control. Typical of these studies is the study of the effect of vortex finder diameter on

the contactor performance (Fig. 9). The efficiency increases as the diameter of the vortex finder increases but the limiting, or flooding, throughput decreases. A performance factor defined as the product of stage efficiency times limiting throughput, does not vary significantly with the vortex finder diameter. Ultimately, a diameter of 0.49 in. was chosen, more to minimize the pressure difference between adjacent stages than to optimize the stage performance. Each point shown on this plot represents an average of about 10 runs made on the contactor with this particular setup.

Another characteristic of the device is shown in Fig. 10 which is a plot of an index to stage efficiency versus an index to throughput. The variable $E/\bar{E}$ is the ratio of the stage efficiency for an individual run to the average stage efficiency for the series from which the run was taken. This plot includes about 550 runs which covers ten separate series and shows that there is little change in stage efficiency with throughput varying from 50% of flooding to flooding. The data on this plot are found to scatter over a range of about 10%.

In the course of the development studies, it was found necessary to compare the performance of similar design configurations. This necessitated data accurate enough to point out the performance differences significantly. Because of the very fast response of the stacked-clone contactor and its rapid approach to steady state, many data were generated and considerable time was devoted to developing experimental techniques which would generate significant data. The large number of runs accumulated (over 2,000 at this time) have shown that perhaps the most important source of error is the location of the equilibrium distribution line. This can be seen on the McCabe-Thiele diagram in Fig. 11. An error of only 1 or 2% in the position of the equilibrium line can cause a 10 to 20% error in the calculated stage efficiency. The McCabe-Thiele analysis is very suitable for immiscible solvents with a single distributed solute. For convenience the development work for the stacked-clone contactor was restricted to such systems.

Toward the purpose of obtaining a characteristic efficiency for a particular design configuration, the following procedure was used: Aqueous and organic solvents were prepared with the solute originally in the organic solvent. During the morning about 10 stripping runs were made transferring about 90% of the solute from the organic to the aqueous phase. This aqueous phase was accumulated and the organic solvent then treated in a peripheral piece of equipment to further strip the solute down to a negligible concentration. In the afternoon the aqueous product from the morning was used for feed for about 10 extraction runs during which the solvent was transferred from the aqueous phase into the organic phase. Care was taken not to alter the composition of either solvent to make certain that the same equilibrium line applied to both the stripping and the extracting sets of runs. A digital computer calculation was then used to adjust a parameter in the equilibrium relationship to yield an average efficiency in the strip runs equal to the average efficiency in the extraction runs. This average efficiency was then used to characterize this particular system, and the technique was known as the compromise K_o calculation (after the distribution coefficient parameter in the equilibrium

relationship). Initially there was no reason to believe that the performance of the contactor in the stripping mode would be the same as the performance in the extraction mode. However, observation of about 50 series analyzed by this technique showed that the adjustment of the equilibrium relation parameter from that obtained by experimental shake-up data was positive as often as it was negative, or that there was no net bias in the direction of adjustment. It was concluded, then, that the stacked-clone contactor worked as well in the stripping mode as it did in the extraction mode.

During the studies to optimize the design of the contactor, uranyl nitrate was used as the solute, distributed between a 1 M sodium nitrate aqueous solution and an 18% tributyl phosphate solution in Amsco (a kerosene-type solvent). When it appeared that no further significant improvement could be made in the design of the contactor (Fig. 12), a program was undertaken to more closely study its other performance characteristics and to investigate its applicability to a variety of different solvent extraction systems. The stacked-clone contactor in its present form must operate with the heavy phase continuous. In the gravity settler at the "top" end, the organic phase breaks cleanly; but the organic phase must be removed from the aqueous phase at the raffinate end by a series of polishing stages. The organic phase throughout the contactor is dispersed in very fine droplets (estimated at 20 microns) which makes the presence of some entrainment inevitable. Figure 13 shows that with a specific set of polishing stages the entrainment increases only by a factor of 2 from 50% to 90% of flooding. With most systems, a very sharp flooding point is observed at which time the organic holdup in the machine increases markedly as does the entrainment. Entrainment can be reduced during normal operation by the addition of polishing stages. Figure 14 shows that each polishing stage reduces the entrainment by the same factor for at least 3 polishing stages.

The stage efficiency for the stacked-clone contactor with the uranyl nitrate system averaged about 70%. It is thought that the stage efficiency is not limited by mass transfer but rather by the effect of backmixing of the phases between stages; that is, some organic phase is carried down the column with the aqueous stream and some aqueous phase is carried up the column at each stage with the organic stream. In order to get 100% stage efficiency it would be necessary to completely separate the phases in each stage such that the stream that left the underflow port would consist of pure aqueous and the stream flowing up into the underflow port would consist of pure organic phase. An implication of this theory is that systems with higher limiting flooding points should show higher stage efficiencies. This generally has been found to be true.

A well-known system that has shown unusually high performance in many different solvent extraction contactors is the hexone - acetic acid - water system. When this system was tried in the stacked-clone contactor, stage efficiencies of over 80% were observed. The McCabe-Thiele plots shown in Figs. 15 and 16 were generated by the digital computer program, and as you will note, have the same equilibrium line. The efficiencies shown, EFFX and EFFY, are different because these are efficiencies from

individual runs rather than the average efficiency in each mode of operation.

Flooding throughputs for various extraction systems are shown in Fig. 17. The hexone - acetic acid - water system is shown with a flooding curve about four times higher than the standard 18% TBP-Amsco system. The other systems shown include 100% tributyl phosphate which is reputedly a very difficult system to run, and mineral oil of about 110 to 120 cp viscosity (equivalent to SAE 20 to 30 motor oil). From the different scales shown on the aqueous phase flow rate and organic flow rate axes, it can be seen that the device performs better at high ratios of aqueous to organic phase flow rate. The dashed lines which show the residence time per stage are calculated by dividing the volume of the physical stage by the total throughput.

A breakdown of the volume of a stage into its different components is shown in Fig. 18. The first column describes the existing experimental model, and the ultimate anticipated volume was projected from estimates of advanced designs. Notice that the connecting lines comprise nearly half of the total volume in the existing unit and that the volume of the pump is of the same order as the volume of the hydroclone cavity. The gravity settling section at the end of the cascade has a greater volume than all of the rest of the cascade combined.

Among the operational benefits from a system that has a small holdup per unit throughput is the fast response time for control. This, of course, could be exploited only with adequate instrumentation. Figure 19 shows the control scheme for the stacked-clone contactor compared with the conventional pulsed column. Both systems control two rates independently, allow one effluent rate simply to overflow, and use the fourth rate to control the position of the interface. While in the pulsed column it is usually the inlet feed rates which are controlled, it was expedient in the stacked-clone contactor to control the aqueous raffinate rate and the organic feed rate independently. The pulse column is usually operated with the effluent raffinate rate controlling the position of the interface, while the stacked-clone contactor was found to perform more stably with the inlet aqueous feed rate controlling the position of the interface. In the pulsed column the location of the interface is determined by bubbler probes which essentially measure an effective density in the top part of the column. In the stacked-clone contactor the position of the interface is not directly measured but is inferred by a measurement of the effective density of the fluids recirculated in the top stage pump loop. These circulation pumps operate on that part of the pump characteristic which gives them essentially a constant head. The pressure developed is therefore proportional to the density and the density is proportional to the amount of organic phase present. Fortunately the location of the interface is proportional to the amount of organic in this stream. Changes in this variable are sensed very rapidly. Figure 20 is a photograph of the chart from the controller of the interface during an imposed step change in throughput. The aqueous raffinate was increased from a flow corresponding to 64% of flooding to a flow corresponding to 87% of flooding. This caused the interface to drop slightly causing the amount of

organic in the recirculating stream from the top stage to increase. The feed valve responded quite quickly and within 6 minutes the system was again at hydrodynamic steady state. About 5 minutes more would be required for the system to come to steady state with respect to composition since the end section turns over about once per minute. Figure 21 is a similar controller chart during a startup. It must be admitted that in this instance all lines were purged and the system was ready to go on stream. It usually takes about 10 minutes to get everything lined out.

The excellent performance of the experimental stacked-clone contactor prompted the development of improvements which would allow the concept to be used commercially. The work to this point had been concentrated on the design of the clone cavity and associated parts along with the performance of this unit. No attention has been given to the design or layout of the pumps, which were standard Eastern Industries 1/8 horsepower pumps. An obvious area for improvement consisted of eliminating the multiple shaft seals associated with the experimental units and a logical answer to include the pumps in the same physical block as the clone cavity. Figure 22 is a drawing of a model of the stacked-clone contactor, presently under fabrication, in which all pumps are driven by a single motor from a single shaft. It is possible to seal this system absolutely by the use of seal wells between stages and a canned motor drive. The critical components are shown in Fig. 23 which is a drawing of a broken and cut-away section of two adjacent stages. The pump shaft runs on graphite bearings which also serve to seal between stages. Since the backmixing rate inherent in the stacked-clone contactor amounts to perhaps 100 ml per minute, interstage leakage as high as 10 ml per minute could be easily tolerated. The pressure difference between adjacent stages is less than 1 psi. Figures 24, 25, and 26 are photographs of the machine components which will go into this prototype model. The components in Fig. 25 include inserts for the polishing section as well as inserts for the extraction section. All impellers in Fig. 26 are identical. This special design minimizes liquid holdup by filling most of the void with metal. It also features a dynamic hydraulic balance to avoid excessive thrust on the bearing.

Figure 27 is a photograph of a test pump with two stages. This unit has been running for over 5500 hours with no detectable wear using the bearings and impellers designed for the prototype stacked-clone contactor. The interstage leakage at this time is only a fraction of a cc per minute.

Since all of the work described has been with contactors using a single line of hydroclones, all essentially the same size, an obvious question is "how can the device be scaled up?" Little experimental work has been done to answer this question. Previous experience with liquid-liquid systems in hydroclones has made it clear that dimensional scale-up is unpredictable. The disadvantageous increase in the ratio of holdup volume to throughput has already been discussed as has the reason for going to the present size of unit. The obvious solution is the use of parallel clone lines. The prototype unit presently under fabrication can be seen to be very wasteful of metal. Figure 28 shows that the capacities could be increased by a factor of 6 by going from an 8-1/2-in.-

diam unit to a 10-in.-diam unit. The pump would not scale up in diameter but only in thickness, and one could extend this principal to a large number of clones as seen by the 23-in.-diam 72 clone illustration. A reasonable limit to the maximum size is probably when the volume of the flow channels to conduct the liquid out to the clones causes the ratio of volume to throughput to pass a minimum. The power requirements for such a unit would increase linearly with the number of clone lines. The length of the unit would remain the same, approximately 10 ft for 18 stages with the associated gravity settler.

The stacked-clone contactor, which a few years ago was more interesting because of its novelty than because of its likelihood for profitable application, has today been developed to a design which produces a very high performance. It has been shown to be usable for a wide variety of solvent systems including very high viscosity dispersed phases which are not easily run in other devices. A model which incorporates all of the pumps within the main body of the contactor and drives them from a single shaft has been designed and is under fabrication. The bearings and impellers for this unit have been life tested and have been found to be more than adequate. And schemes for scale-up up to perhaps 72 gallons per minute throughput now seem plausible.

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Fig. 1. Liquid Flow Pattern in Hydroclone.

Fig. 2. Functional Parts of the Stacked-Clone Contactor.

Fig. 3. Stacked-Clone Contactor Cascade.

Fig. 4. Organic Feed Stage and Polishing Section.

Fig. 5. Assembled 11-clone Contactor.

Fig. 6. Contactor Component Parts Shown Separately.

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Fig. 7. Shapes and Underflow Chamber Evolution of the Stacked-Clone Contactor.

Fig. 8. Earlier 7-clone Contactor Assembly.

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Fig. 9. Effect of Vortex Finder on Throughput and Efficiency: Mark VI Stacked-Clone Contactor.

Fig. 10. Per Cent Flooding vs $E/\bar{E}$.

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Fig. 11. Operating Diagram for Stacked-Clone Contactor Runs.

Fig. 12. Stacked-Clone Contactor.

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Fig. 13. Entrainment of Organic Solvent in Raffinate of Stacked Clone Contactor.

Fig. 14. Reduction of Entrainment by Polishing Stages.

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Fig. 15. Aqueous Phase Conc., X, vs Organic Phase Conc., Y.

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Fig. 16. Aqueous Phase Conc., X, vx Organic Phase Conc., Y.

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MARK X, STAINLESS-STEEL, 11-CLONE CONTACTOR
INCLUDING 4 POLISHING CLONES

Fig. 17. Effect of Relative Flow Rates on Flooding in the Stacked-Clone Contactor.

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	VOLUME (cc)	ULTIMATE ANTICIPATED VOLUME (cc)
HYDROCLONE CAVITY	34.5	34.5
UNDERFLOW CHAMBER	10.1	10.1
FEED BLOCK (PLENUMS, PORTS, AND DUCTS)	23.8	23.8
PUMP	41.0	25.0
PUMP CONNECTING LINES	<u>103.0</u>	<u>21.0</u>
VOLUME PER STAGE	212.4	114.4
PRODUCT-END SETTLING SECTION	2490.0	3000.0

Fig. 18. Volumes of Components of Mark X Stacked-Clone Contactor.

Fig. 19. Comparison of Control Systems for Stacked-Clone Contactor and Pulsed Column.

Fig. 20. Response of Interface Control to a Step Change in Aqueous Effluent Rate.

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(FROM A SHUT DOWN CONDITION WITH THE STACKED-CLONE CONTACTOR FILLED WITH AQUEOUS FEED, ALL PUMPS WERE STARTED AND THE SOLVENT FEED AND AQUEOUS EFFLUENT QUICKLY SET AT FLOWS CORRESPONDING TO 70% OF FLOODING AT $A/O = 2.5$) SYSTEM: MINERAL OIL— $0.01M$ HNO_3 .

Fig. 21. Response of Interface Control at Instantaneous Startup.

Fig. 22. Stacked-Clone Contactor Prototype for Radiochemical Application.

Fig. 23. Integral Pump Prototype Stacked-Clone Contactor Cutaway
Illustration of Adjacent Stages.

Fig. 24. Typical Extraction Stage Body of the Combined Pump-Clone Contactor.

Fig. 25. Inserts for the Pump-Clone Contactor.

Fig. 26. Pump Impellers.

Fig. 27. Prototype Pump Test Assembly.

Fig. 28. Scale-up Principle for Stacked-Clone Contactors.

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