STATE OF THE ART
AND
FUTURE DIRECTIONS IN SOLVENT EXTRACTION

**PROCEEDINGS
OF THE THIRD INTERNATIONAL
SOLVENT EXTRACTION WORKSHOP 2003**

**AUGUST 31- SEPTEMBER 3, 2003
DIGBY, NOVA SCOTIA,
CANADA**

Organized by Dr. Gordon M. Ritcey

**Sponsored by the International Committee for Solvent Extraction Technology
(ICST)**

Workshop Web Site: http://sxworkshop.tripod.com

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FORWARD

The following is a summary of the Solvent Extraction Workshop'2003 that was held August 31 – September 3 in Digby, Nova Scotia, Canada. The Workshop, which was the third such meeting, was again sponsored by the International Solvent Extraction Committee (ISEC). The workshop, which was by invitation, covered all aspects of the solvent extraction process,

This SX Workshop was held 3 years after the second workshop in Banff, Alberta, and again about half-way between the previous International Solvent Extraction Conference (ISEC) in Capetown, ISEC'2002, and the next meeting, to be held in Beijing, China, ISEC '2005. The purpose of these Workshops is to bring together many of the experts in solvent extraction to identify and to discuss the various problem areas in this unit process. The recommendations would provide the many researchers and operators throughout the world with good project ideas that could result in significant reductions in capital and operating costs of solvent extraction plants. Although the previous two Workshops were successful in 1997 and 2000 in Banff, it was decided to have the 2003 Workshop on the seacoast, at Digby, Nova Scotia.

Again, this workshop was planned not as the usual, formal, conference, but instead was styled after the very successful and informal Gordon Research Conferences that have been held in the USA on various aspects of chemistry and engineering.

The list of possible invited experts for such a workshop was assembled by various members of ICSE. If the workshop was to be successful, the total attendees would be limited to about 75. In this third Workshop, the participation was 38, of which 21 were repeats. This number was down slightly from the second Workshop. Actually the smaller number contributed to more opportunities for input into the discussions. The economic climate, the scare of SARS, the economy and the world terrorism all contributed to the smaller number of participants.

It was hoped that the invited specialists would recognize that participation would be useful to the solvent extraction community in general, as well as an opportunity to personally benefit from the meetings. Invites included those from chemistry, chemical engineering, process design, engineering contractors, and operating plants. As in the first two workshops, it was anticipated that the Solvent Extraction Workshop'2003 "experts" in the areas of R & D, engineering and applications would:

1)   Critically review the individual areas of concern in the consideration of solvent extraction from R&D to its industrial scale-up to plant processing;

2)   Provide a closer interaction between chemistry-engineering-process development-plant design and construction then is possible in the usual, large international meetings;

3)   Improve the communication between the R&D scientists and engineers and the engineering contractors to optimize the design of future solvent extraction operations;

4)   Transfer the conclusions of this meeting to ISEC 2005, thus providing some guidance to future R&D and plant design; and,

5)   Would provide a document for wide circulation amongst practitioners, possibly by publishing in "Hydrometallurgy".

The **_objectives_** of this workshop were similar to the previous Workshops:

1)   **_Address and critique_** the various areas of the SX process, including:

a) Fundamental research in chemistry & chemical engineering

b) Flowsheet development (chemistry, chemical engineering, metallurgy) through to piloting to obtain preliminary design and cost data

c) Engineering design, control, plant design and plant construction

d) Plant operation (problems and solutions)

2)   **_Determine where there are gaps or flaws in our knowledge_** so that:

a) Additional fundamental research projects would be identified and carried out;

b) Possibly some on-going fundamental research may be identified as not generally applicable to improving the process in the long term;

c) Identify where improved chemistry, extractants, contactors and control could be developed or improved to enhance the overall operation and economics in the process and plant design; and,

d) An improved understanding and communication between chemists-engineers-engineering companies will result in improved plant operations, thus reducing the many costly operating problems of plants.

The meetings took place over a 4-day period, although the first day, Sunday, was really to arrive and meet each other socially at a reception.

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The format comprised an informal technical session in the morning, followed by lunch and then break for the afternoon. This permitted the attendees to visit the area for sightseeing, or participate in sporting activities of their choice. Following dinner, the evening sessions commenced.

On Monday, the first part of the morning was devoted to the introduction of the workshop, followed by 5 short 15-minute Plenary presentations in the areas of Chemistry, Chemical Engineering, Process Design, Plant Design, and Plant Problems. The various items of concern, some new and others left over from the previous Workshops were distributed to all attendees prior to the Workshop.

Following the Plenary presentations, the participants broke into 2 discussion groups—a large group comprised of chemical engineering, process design, plant design and plant practice. The subsequent group workshops that morning and evening, Tuesday and Wednesday morning dealt further with the list of concerns in more detail. The workshop closed late Wednesday afternoon. Usually, a summary of the group discussions are presented, but insufficient time was available Wednesday afternoon.

Like any technical meeting, there were a number of invites who were unable to attend due to other commitments, illness prior to the meeting, and also some who were assigned other responsibilities in their respective organizations, as well as SARS etc. mentioned earlier. This was indeed unfortunate. However, those that did attend were rewarded, I believe, in the useful discussions that resulted with their participation. The venue of the Digby Pines Resort proved excellent, and the weather contributed to sunny days that week. Many of the participants were able to tour the area—fishing, hiking, cycling, whale watching and general sightseeing.

Gordon M. Ritcey, SX Workshop '2003 Chairman

SOLVENT EXTRACTION WORKSHOP'2003
DIGBY, NOVA SCOTIA,
AUGUST 31 - SEPTEMBER 3, 2003

PROGRAM

Sunday August 31

Check in at the Pines Resort Hotel	
1500-1630	Registration – Foyer
1700-1830	Reception - Living Room Lounge Bar
Dinner "on own"	

Monday September 1

830	Registration Continues for late arrivals outside Salon A in the Conference Centre
900	Opening Remarks - Salon A in the Conference Centre (Gordon Ritcey, Geoff Stevens)
915	Plenary Presentations - "Challenges in Solvent Extraction"
0915-0930	Chemistry (Mike Cox)
0930-0945	Chemical Engineering (Geoff Stevens)
0945-1000	Process Development (Kathy Sole)
1000-1015	Plant Design (Mark Vancas)
1015-1030	Plant Problems (Gordon Ritcey)
1030	Break _ Coffee/Tea In Foyer of Conference Centre (Digby Hall)
1100	Workshop Sessions (Rooms A & B)
1215	Break for Lunch ("on own")
Afternoon – Free	
1900	Workshop Sessions (Rooms A & B)
2030	Break _ Coffee/Tea
2100	Close of Sessions

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DIGBY, NOVA SCOTIA
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PROGRAM (continued)

Tuesday September 2

900	Workshop Sessions (Rooms A & B)
1030	Break - Coffee/Tea
1100	Workshop Sessions (Rooms A & B)
1215-1330	Lunch ("on own")
Afternoon – Free	
1900	Workshop Sessions (Rooms A & B)
2030	Break _ Coffee/Tea
2100	Close of Sessions

Wednesday September 3

900	Workshop Sessions (Rooms A & B)
1030	Break- Coffee/Tea
1100	Workshop Sessions (Rooms A & B)
1215-1330	Lunch provided for Workshop Participants (Dining Room)
1330	Wrap up session _ Room A *Note: This final session will be held immediately following lunch, instead of in the evening. This will give those that depart later on Wednesday the opportunity to participate. This session will be devoted to summary presentations of the individual work groups.*
1500	Break
1630	Close of Workshop

WORKSHOP DISCUSSION AREAS

CONCERNS THAT NEED TO BE ADDRESSED

The following are concerns in the SX process that hopefully would be addressed in Workshop 2003. These concerns are a follow-up on Workshop 2000 together with additional concerns expressed by the participants prior to the meeting in 2003. The concerns are listed in no particular order of priority.

CHEMISTRY
1) Reagent degradability—causes & mechanisms
2) Chemistry/kinetics/viscosity & physical aspects changing as loading occurs
3) Treatment of fouled organic
4) Dependence on design of the aqueous media: SO_4, Cl^-, NH_3, regarding degradation, contactor, etc
5) Use of chloride leaching and/or in SX process—advantages/disadvantages
6) Speciation – what philosophy and techniques are required
7) Crud – understanding the causes and develop preventative options. Can formation be predicted?
8) Chemical influences in coalescence – is it more important than the physical influence?
9) Multi-component systems—precautions required, and on-line detection of critical fouling due to a second extractant
10) Materials synthesis in SX
11) Interfacial chemistry
12) Kinetics
13) Extractants, modifiers, diluents

CHEMICAL ENGINEERING

1) Drop size vs. extraction system –prediction for optimum kinetics/mass transfer
2) Do we have to recycle the minor phase? What are the advantages/disadvantages? Is it a question of adequate mixing (mass transfer) or phase continuity (solvent losses)? Effect also of drop size & therefore coalescence.
3) Guidelines to running small columns to provide adequate scale-up for engineering. Samples and measurements required? Mixing criteria?
4) Measurements of plant performance, e.g.:
    a) Interfacial tension
    b) Surface tension
    c) Density
    d) Viscosity, etc.
5) Measurement/modeling of droplet breakage and coalescence
6) 2-phase flow
7) Coalescence & modeling
8) Novel SX processes
    a) reversed micelles

        b) microemulsions
        c) colloidal suspensions

9) Interfacial phenomena
10) Modeling of liquid-liquid dispersions in process design
11) Metal extraction from dilute solutions
12) Use of lab techniques & computer simulation to save on running-in of pilot plants
13) Pilot plants vs. demo plants in columns & MXS.
14) The use of columns in hydrometallurgy
15) How to decrease entrainment in plant effluents and what is the minimum level of entrained solvent in the aqueous wastes.
16) Modeling of droplet breakage and coalescence
17) 2-phase flow
18) Measurement coalescence & modeling

PROCESS DESIGN / DEVELOPMENT & OPERATIONS

1) Reagent degradation – causes, prevention, treatment, regeneration?
2) Impact of crud on plant and environment. What is the update on plant operation?
3) Cross contamination in more than a single solvent extraction circuit or in the use of mixed anion (SO4, Cl) circuits
4) Solvent losses in plants - % breakdown for each and what are the possible new recommendations
5) Alternative SX contactors to MXS, e.g., columns, in-line mixers, etc.
6) Bench-scale was considered in reasonable detail in 2000. Are there additional points that should be added? One concern is the predictability of plant problems over time with recycle (build-up of poisons).
7) What type of mixing tests should be done in early development to predict mass transfer, dispersion, coalescence as a function of drop size, interfacial tension, etc?
8) Is there a future for solvent-in-pulp processing in order to reduce the high capital and operating costs of the liquid/solids separation? In this area, the use of other contactors (than MXS) would be the driving force to success.
9) Protocol for the treatment of effluents, wastes, residues – all to comply with environmental guidelines. Will the process be much different than treating ore leach solutions/ e.g., use of other unit process such as IX, RO?
10) In the use of other types of contactors, what information is available on the treatment of solutions for the recovery base metals, precious metals, rare metals, rare earths, etc.?
11) Physical chemical aspects
12) Basic data required
13) Scale-up problems
14) Linking of 2 circuits
15) Problems in Cu, Co, Ni, U
16) 3rd phase; 3rd phase and acidity; 3rd phase and sludge; 3rd phase and reagent loss
17) Reagent loss and how to decide on the most suitable concentration of modifier in the organic phase

18) The maximum O/A ratio in extraction
19) Aspects of high concentration acid stripping (U system)
20) Solvent recovery equipment (after settlers, flotation, cyclones, etc. How well do each work in plant experience?
21) Interface detection and control instrumentation—what has worked and what has not been successful
22) Contamination of circuit organics, particularly copper SX circuits, but also circuits using amines
23) Clay treatment
24) Crud removal
25) Analyses/quantification of surfactant presence
26) Organic health indicators

PLENARY PRESENTATIONS

SOLVENT EXTRACTION CHEMISTRY
Michael Cox

Opportunities and Challenges

    I.   Reagents
    II.   Analysis
    III.   Novel Systems

I Reagents

- New reagents or novel uses of existing extractants
- Use of mixed systems
- Kinetics
- Modifiers
- Degradation

1) Need for new reagents?

- Hydrometallurgy
- Nuclear applications
- Environmental use

2) Mixed Systems

- Synergism
- 'Salt extraction' – 'MV'

3) <u>Kinetics</u>

- Interfacial effects
- Increased rates of extraction / stripping

4) <u>Modifiers</u>

- Various roles

5) <u>Degradation</u>

- Long term problems
- Nature and effects
- 'Clean-up'
- Reagent 'regeneration'

<u>II Analysis</u>

1) <u>Organic phase</u>
2) <u>Inorganic phases</u>
- Speciation

<u>III Novel Systems</u>

1) <u>Non-dispersed systems</u>

- Surfactant (emulsion) membranes
- Polymer supported membranes
- Impregnated systems

2) <u>Micellar extraction</u>

3) <u>Aprons</u>

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**CHEMICAL ENGINEERING
FUTURE DIRECTIONS**
Geoff Stevens

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Thermodynamics and Equilibrium

- Data bank for equilibrium, thermodynamics and physical properties
- Models for prediction of thermodynamic properties
- Fluid structure and its influence on separation, micelles etc

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Kinetic and Non Equilibrium Processes

- Kinetics models for metal transfer processes including influence of other species
- Role of impurities
- Multi-component systems

Contactor Design

- Plug flow models – [McCabe-Thiele]
    - Limited accuracy
    - Limited ability to predict performance at other conditions
- Axial dispersion models
    - Still not used for design
- Computational fluid mechanics models
- Pilot plants and scale-up techniques

Interfacial Phenomena

- Drop coalescence and breakage
- Phase continuity

Modelling and Control of Processes

- Modeling and simulation
- Sampling
- Verification on continuous circuits
- Process dynamics and control
- Start-up

New Equipment

- Hydrometallurgy
- Environmental
- Chemical and Pharmaceutical

CHALLENGES AND PROBLEMS OF PROCESS DEVELOPMENT
Kathy Sole

Challenges of Chemistry

- Viable flowsheets for nickel laterite processing
- Manganese from zinc electrolytes
- Processing of high acid solutions
- Vanadium / chromium separation

- Solvent-impregnated resins
- Membrane-assisted processes
- Molecular recognition technologies

Modeling challenges

- Good predictive and simulation capability for copper extractants
- Less so for other extractants

Process Considerations

- Position of SX in circuit
- Solvent exposure to undesirable components
- Solvent cost and resilience
- Feed to SX plant
- Raffinate and loaded strip liquor
- Control strategy

Piloting Considerations

- How long to run?
- Behaviour of trace impurities over longer term
- Rheology and physical data
- Variations in feed composition
- Difficult to test hydrodynamics properly
- Site-specific issues – water quality, lime, temperatures, climate, *etc*.
- Neutralisation NH_3 or NaOH, mechanism of introduction, *etc*.
- Sampling and analysis – detection limits
- Materials of construction
- Crud handling, clay treatment, organic recovery

PLANT DESIGN CONSIDERATIONS
Mark Vancas

Design Criteria

- Laboratory and pilot plant test results
- SX contactor selection
- Scale-up

Plant Design Considerations

- Location and plant layout
- Piping design particularly around pump-mixers

- Level of automation
- Cross-contamination of series circuits
- Materials of construction
- Reduction and removal of static electricity
- Fire and safety
- Environmental considerations
- Climatologic concerns
- Crud
- Operability
- Maintenance
- Client desires
- Niceties and necessities
- Client knowledge
- Operating staff knowledge and capabilities

CHALLENGES IN THE PLANT OPERATION AND SOLVENT LOSSES
Dispersion/Coalescence/Emulsions/Crud
Gordon Ritcey

Solvent Losses

- Solubility
- Entrainment
- Stable emulsions
- Crud
- Vaporization
- Misting
- Sampling & spillage

Major Losses Affected by:

- Equipment selection
- Plant design
- Mode of operation
- Controls on process

Sources of Problem:

- Over-mixing (2-stage, high shear, McCabe-Thiele for design vs. plant operation)
- Settler design inadequate for type of emulsion (linear velocity)
- Surfactants
- Poisons (cations, anionic species, e.g. amphoteric compounds, organic acids, surfactants
- Emulsions (slow breaking and misting effects)
- Crud (dust, suspended solids, precipitates in one or both phases)

- Cross-contamination in multi-extractant plants

Minimizing of Problem

- Improved clarification in MXS plants, but not a problem in low shear plants
- Cover of SX circuit to minimize dust entry
- Controlled mixing (time & McCabe Thiele)
- Selection of optimum contactor (in-line mixer, column)
- Tests for need for a diluent wash of PLS
- Diluent wash of raffinate feed to 2nd circuit
- Tests for solvent fouling and subsequent continuous treatment of solvent bleed stream for removal / control of poisons

Plant Improvement

- Decreased solvent losses
- Decreased adverse impact on environment and hazards to workers
- Decreased operating costs
- Improved products grade through control of impurities in PLS, poisons on loaded solvent and introduction of a scrub stage following extraction
- Improved throughput per cross sectional area with decreased stable emulsions

WORKSHOP DISCUSSIONS

CHEMISTRY GROUP
Reported by M. Cox

1. New reagents:

- Need to define a market and its overall process requirements; difficult to break into an established market where the operators are largely satisfied with the existing process, e.g. tank-house bleeds.
- In such a case, the new process must convey defined advantages in cost, product quality and ease of operation.
- In addition, any new compound requires extensive and expensive testing to meet toxicological and environmental regulations.

2. Potential areas for application:

- Nuclear waste: Still potential for new extractants.
- Environmental: treatment of dilute streams; good selectivity over innocuous species, e.g. Ca, Mg, Na. K, etc. Possible hybrid processes, e.g. RO + SX. Need to produce drinking water quality raffinate.
- Specific targets: concentration of dilute mineral acids for acid reuse; e.g., high purity vanadium for batteries.

- Interesting developments in macrocyclic reagents, e.g. molecular recognition technology; crown ethers, 'lariat ethers' – but cost and stability could be a problem
- 'Salt extraction' with mixtures of acidic/chelating and basic (amine) functions – could be useful to produce 'process waters' from effluents.

3. If not new reagents – reagent mixtures

- Synergism could now be accepted by operators as appropriate techniques to monitor organic phase are available and operators are comfortable with phase formulations consisting of mixtures of extractant(s), e.g. aldoxime and ketoxime mixtures, and modifiers.
- Thus, instead of 'new' compounds novel mixtures of existing compounds to produce processing advantages might be more rewarding.
- Such mixtures of existing reagents would not require toxicological and environmental testing.

4. Degradation

Caused by reactions on the organic phase caused by biological, chemical and environmental factors.

- Extent depends on nature of extractant, diluent, modifier, metal(s), anion(s) and impurities present.
- Extractant - Hydrolytic oxidation processes most common.
- Diluent: - Oxidation to carboxylic acids, may be metal catalysed; choice is important – aromatics more stable than aliphatic but also disadvantages.
- Metal - Catalytic effects, potential change of oxidation state, combination of Eh-pH.
- Anion - Nitrate and mixtures of nitrate/chloride are particularly damaging.

Degradation products will tend to be surface active and therefore affect the overall process and generally promote crud.

- Biological degradation - Minimized by good housekeeping and hygiene,
  Clean up by periodic 'shock use' of biocide to remove bacteria.
- Environmental degradation - U.V. degradation/air oxidation, care in reuse of organic phases from raffinate ponds, etc.
- General clean up - Clay treatment often satisfactory although carbon columns also used.

5. Crud

- Crud requires surfactants and particulates, e.g. clay/inorganic solids, dust, etc.
- Generally seems to be less of an operating problem, 'a little crud seems to be beneficial', uranium circuits more persistent crud probably from more aggressive leaching.
- Purity of extractants will influence amount of surface-active impurities.

- Volume of crud seems to depend on 'housekeeping':
    - Absence of 'carry-over' pf surfactants from other process operations in circuit;
    - Absence of humic/fulvic acids from leaching;
    - Care in reuse of water from tailings pond.
- Where surfactant carry-over or propensity for crud formation a problem then diluent wash of aqueous phase before solvent extraction often beneficial – diluent regenerated by caustic wash.

6. Dual SX circuit operation

- Vital to keep both circuits separate to minimize reagent crossover between circuits.
- Precautionary treatment a diluent wash of raffinate between streams followed by carbon column with stream stripping to recover organic phase.
- Carefully consider the order in which extractants used.

7. Ionic Liquids

Replacement of organic phase with water immiscible ionic liquid.

- Potential for environmental and process improvements.
- Current disadvantages: Cost of ionic liquids very high;
    a) Selection of ionic liquid to ensure hydrolytic stability;
    b) Variation in viscosity with water take-up affects mass transfer;
    c) 'Ion exchange' between extracted species and components of ionic liquid.

8. Micelles

- Formation of reverse micelles in organic phase a function of nature of surfactant and concentration.
- Extractants are surface active and form reverse micelles depending on pK_a of extractant, pH of system and concentration.
- Micelles can transport water and other ions into the organic phase within the micelle, reducing selectivity and contaminating subsequent aqueous streams.
- Eventually aid third-phase formation.
- However, micelles do not seem to significantly affect SX operations.

9. General conclusions

- Reagent synthesis: carefully consider targeted species;
    - How does the proposed extractant improve existing process;
    - Cost vs. value of product.
- Operators: Many problems stem from plant house-keeping/hygiene.
    - Care over reuse of organics from spills and ponds;
    - Consider diluent wash of feed to reduce crud/degradation, and raffinates between different circuits;
    - Care over recycle of water from tailings pond.

PROCESS AND PLANT DESIGN, AND PLANT PRACTICE
Reported by D. Thibault

1. Drop size vs. Extraction Systems --sizing of system

- Columns / inline mixers—control drop size

- Use of drop size measurements to design size of plant
  Tip speed 4-5 m/sec related to entrainment loss
  The amount of entrainment may not be directly related to the tip speed; the degree of turbulence or the amount of energy used for mixing should also be considered.

- The longer the mixing time at high shear the worse the problem of small drop sizes becomes as regards coalescence and entrainment losses. The mix time, throughput and mix intensity may vary.

- Measure of mass transfer coefficient can be important but may be difficult to measure directly from test programs.

- Mass transfer has a major effect on efficiency (may change within sections of column).

- It is difficult to define mass transfer coefficient for a gas-liquid system. How important is drop size to the design? In practice, residence time is used to size equipment and the drop size is not commonly used.

- The size of the bubble should be determined for relative correlation of equipment performance. What do we measure and how is this measurement used to determine the efficiency of separation? How accurate is scale-up? The use of bubble size and method used to determine the bubble size are not considered very accurate.

- The use of a variable speed mixer would permit the adjustment of drop size. This can be accomplished without prior data.

- The data validity depends on a number of parameters, including the need to acquire major data for many factors that affect drop size; (i.e. geometry of column, internals design and materials of construction, impurities and surfactants). To achieve an effective contactor design, these factors are included in the variables that are important.

- There are 2 groups of thought on the subject of drop sizes: academics and plant operators. It is probably unlikely that operators will fund drop size measurements research for design optimization.

- There is a relation between drop size and kinetics of mass transfer.

Need to define this important aspect in pilot plant programs. Plant design should not proceed without the application of good engineering principles

- If drop size is known, how will that data be used in the plant design? This parameter will vary frequently.

- How is drop size determined in the plant? Measurement in the plant is probably not feasible. Knowledge of how to change the drop size in the plant is an important factor in the design and for the knowledge of the plant operators in operating the plant more effectively. A change in operating parameters may not always change the drop size.

- The impellors design and speed may provide a wider distribution of drop sizes

- In-line mixers may provide a narrow drop size distribution; however the cost of extra pumps for use of in-line mixers must be recognized

- Droplets measured in operation of in-line mixer pilot plant showed a correlation of decreasing drop size with increased mass transfer as well as decreased coalescence rate.

- Problems in Cu circuits are not always caused by non-idealized design but often by mode of operation as effecting mass transfer.

- Processes where continual neutralization is required are difficult to control drop sizes due to localized precipitation

- Generally, with sufficient information, drop size can be predicted.

2. Columns – Guidelines

- The column diameter is very important in the decisions for scale-up, for wall effects are serious in the engineering design. Depending on the column design (e.g. such as axial and back-mixing) the minimum column diameter for safe scale-up will differ. For example, in a Bateman pulse column, 80 mm or more are required for accurate scale-up. A pulse sieve-plate column has been successfully scaled from a 50 mm diameter pilot column. Most centrally-agitated columns require possibly 150 mm diameter for successful scale-up. Parameters required for scale-up include flooding, flows, phase ratios, solvent concentration, viscosities, densities, mode of operation such as phase continuity, energy for mass transfer (low shear vs. high shear), and temperature. The choice of extractant and the diluent selected also are important factors in the successful testing and scale-up.

- In the chemical industry, tests are performed using small columns with a diameter as low as 32 mm. The capacity of the unit will be dependent on the reaction and methods used to induce mixing.

- For the metals industry, a Bateman pulse column, 3-inch (75 mm) diameter has been successfully scaled up to 2.5-3 ft (75-90 cm) diameter. In stirred columns, an increase in height will impact on the axial and back mixing characteristics, thus affecting scale-up.

- Comparing 1-inch to 6-inch diameter columns, the larger diameters are used for the study of the hydraulics of the system, and the smaller diameters for verification of the chemistry. In one present study is the measurement of flow patterns in columns during the operation.

- With experience, the management must justify efficiency accuracy of the initial size of the unit (pilot unit) required relative to the capital and operating cost estimates. Usually a conceptual estimate is completed before pilot plants are run. Occasionally the pilot plant may not perform to expectations or the process is not economically viable. Management will not support the cost of the pilot plant if the capital investment cannot be justified.

- There is a requirement to make the initial estimate of the number of columns required in a new process based on basic lab information; then make estimates of the minimum and maximum sized based on total flows. The "risk" to proceed with pilot evaluation can then be determined. As regards the diameter to test, there is often not much saved by running a small diameter column except in the case where the tests are not at an operating site and solution has to be shipped to where the test site is located.

- To pilot and evaluate various columns, because there are many designs available, would be too expensive. Therefore, an early decision has to be made as to which column(s) design to study. The determination will be based on the solution type, extractant type and concentration, phase ratio required, kinetics, ease of phase disengagement following mixing, number of stages required, and perhaps area or height restrictions.

- Pilot column design should include provision for sampling the column length. Glass columns permit visual examination of the physical process. Physical analyses may include: temperature, flooding, phase disengagement, surface tension, viscosity, and interfacial tension. The physical measurements together with the mass transfer analyses will provide information to assure the contactor viability selection for scale-up. The diluent choice will also be an important factor in optimization.

- "Materials of Construction" selection is an important aspect relative to such as static electricity that may be caused at high velocity through a "pipe". Aqueous

continuous may be preferred to organic continuous as regards minimizing static problems, although reduction in emulsions and entrainment may favour organic continuous.

- Various column designs have been used throughout the chemical, petrochemical, pharmaceutical, and agriculture industries for many decades. The nuclear industry, particularly in the refining, have used sieve-plate pulse columns for more than 50 years, and various designs have been used in the recovery and separation of certain rare metals (Zr-Hf; Nb-Ta). The sieve-plate pulse columns were used for the initial Co-Ni separation plant in the 1960's as well as applied to the recovery of U and Cu at that time. Over the past 25 years the sieve plate pulse columns have become more common in the treatment of mine leach solutions for the recovery of U. More recently, the Bateman disc-and-donut pulse columns have been installed for the recovery of U, with Co and Cu the next metals to be recovered. Combining extraction and stripping in a single column appears to be a significant savings in capital and operating cost, according to work by Bateman.

3. Recycle of the Minor Phase

- The concept of minor phase recycle was initially adapted by uranium plants, followed by the Cu operations. The purpose was to maintain a specific phase continuity to obtain optimum mass transfer as well as to obtain optimum coalescence conditions. For the Co-Ni separation in the 1960's when sieve-plate pulse columns were initially used, minor phase recycle was not considered, as high phase ratios of up to 30:1 could be used without a problem of maintaining a particular phase continuity.

- Regardless of drop size the phase ratio is important in the design to obtain optimum mass transfer. Mixer settlers usually will "flip" the phase continuity if the phase ratio is much above 3:1 (and sometimes less). Pulse columns have been demonstrated to be able to maintain phase continuity even at 50:1 ratio. Above that ratio, it may be difficult to achieve

- It may be possible to use a very high phase ratio if high shear is not used in the contact of the 2 phases. This has been found possible in the use of in-line mixers, where there is no high shear and no recycle is required.

- To control the amount of solvent entrainment losses, it may be necessary to recycle the minor phase. Phase continuity is determined by the direction of mass transfer. That is, in extraction into the organic phase, the phase continuity as regards the chemistry will be optimum at organic continuous.

- Phase ratios play a part in the formation or prevention of gels, and thus is an important aspect in plant design and operation of the contactor.

4. Two-Phase Flow

Within the group there was a limited discussion on two-phase flow. It was noted that the modeling of two-phase systems does not predict the operating sytems and thus further work is required to improve on the reliability of such modeling.

5. Extractant Development

There was a limited discussion on the development of new SX technologies or use of new extractants. Some of the participants expressed interest in the development of SX circuits for the following applications:

- Separation of lithium from sodium-rich brines.

- Optimum separation of niobium and tantalum using tributylphosphate.

- Optimum separation or removal of chromium from vanadyl sulphate; for high purity redox battery markets.

- Purification or retreatment of process water using SX technology.

- Treatment of tank house bleeds; which would enable solution recycle or optimization of water balance.

6. Synergism

- The possibility of the use of synergism was introduced in the mid 1960's; mass transfer and kinetics can be positively affected.

- Often perceived as a problem if introduced to a plant due to non-equal losses of the 2 or more extractants.

- Some early problems of analysis of constituents were encountered

- Must demonstrate an economical benefit by the introduction of a synergistic extraction system.

- Some on-going work is in progress for such as Co, Mn.

7. Bench - Pilot Scale Tests

- Reagent suppliers have developed models for bench tests, but are not dependent on the type of mixer used.

- For sizing a column; equilibria data for stage determination; density, etc. are obtained through running of tests to steady state conditions in a small column to

identify continuous phase effect and other parameters, and to assess the potential for the process as well as the possible choice of a column. This is followed with a pilot program in larger columns where confidence in scale-up is attained with 100 mm diameter columns. Present pulse columns are scaled up to 4.5 m diameter.

- Continuous testing is usually performed in small units with total flows of perhaps 500 ml/min. Such a small scale will only prove the chemistry, verifying the bench data. The wall effects are so great in the small size mixer settlers that settling tests and therefore reliable data on entrainment losses, recycle streams etc are difficult to obtain.

- Measurements of phase disengagement rates can be determined in graduated cylinders. Better information is obtained through the running of deep settler tests in which settler sizing can be calculated, as well as optimizing the mixing conditions as regards the phase continuity.

- A demonstration plant may be required by the company, and may be 5-10% the size of the final plant. Also, the demonstration plant may run for perhaps 5 years to convince management of the economic viability of the process. With such a size plant, there will be product produced for evaluation by potential buyers, and additional sufficient product is produced to help pay for the demonstration plant costs.

- The petrochemical industry design systems from computer models using physical-chemical parameters. Does this mean that the computer models may be used to design SX circuits (such as copper systems)? It was concluded that models may be used for specific situations but designers are not prepared to use models to design commercial plants.

- Test programs may also include the running of pilot plants systems to assure no degradation of the organic. This will require extensive operating time and monitoring of relative changes in performance. The test programs may include the assessment of performance relative to change in organic concentrations and the O/A ratio. Pilot plants are also used as training facilities for technical personnel as well as for an examination of the safety issues. The design of SX circuits should be based on the participation of operations (operating staff) during the pilot programs.

- There is a risk in going from bench data to a full-scale plant without the intermediate piloting stage. Funding of a plant by the banking community is facilitated when pilot data are available. Models are required, and are valuable in assessing the flexibility of plant design.

- Often a project is recommended to management prior to calculating the economics or capital investment requirements. The cost of the project from piloting to decommissioning should be defined at the conceptual stage of the plant

design. A pilot program may cost $2-3 million /year and the cost of the commercial plant may be around $10 million. As an integral part of the "Quality Management Plan" the costs of each stage must be quantified; the economic criteria should be defined for the pilot program to assure economic viability.

- During piloting, the need to for additional bench scale testing may be defined to solve technical problems with system performance. The "Owner" of the project may say "too expensive" or "too much time is required" and may not agree with extensive testing to improve on technical viability. Also, a company acquiring a loan for commercial production will require a proven technology. In most cases a funding institution (banks) will not loan money for a technology that is not considered proven; and solvent extraction may be considered an un-proven technology. In such a case, pilot programs may be run to serve the requirements of the funding institution and CEO's may dictate the scope of the pilot program.

- In some cases a pilot plant may be constructed before the flowsheet is proven. One pilot plant was mentioned that had a flow capacity of 133 L/h that could produce 500 T product annually. But this large pilot plant was build prior to any bench design data. So the company went to bench tests, and subsequently built small continuous circuits to establish the operating parameters.

- Often there are serious cost overruns in the running of a demonstration plant. One such plant was noted and the question of why such a problem occurs was asked.

- Solvent extraction in the organic and pharmaceutical industries is usually in small plants, and may even be batch processes. Therefore, there is no accumulation of crud. Because of the size, it is often not worth running a smaller circuit (pilot plant), but cheaper to run the plant as a pilot plant.

- In the chemical industry, accountants consider that possibly the product will not sell (based on only bench data), and therefore there is the need to confirm data in a pilot plant program It is recognized that it is a battle to keep plants operating with new technologies, and both economic and product market acceptance needs to be confirmed with pilot programs.

- In oil refineries, the efficiency of aromatic/aliphatic separations in columns is supported by the use of pilot systems. New feedstock extractions and the efficiency of separation are evaluated using 150 mm diameter glass columns. Glass columns are generally used to provide visual observation of the separation.

- The feasibility study for a client as regards a pilot plant will depend on the process technology that has been proven, i.e. Cu plants already in production. There have been examples of mixer settler plants being built (i.e. some Cu operations) in which no previous piloting had been performed, resulting in serious operating problems and therefore extremely high operating costs. Thus

some companies have taken a risk based on beaker tests (and perhaps only a computer model!) and built a plant, often with sad results.

- Use of pilot plant and accumulated data are necessary to provide reliable design and cost estimates, for capital costs are an important goal in the ultimate decision to plant construction. Parameters to investigate include: change in feeds; retention time; relevancy of the drop size to performance. The pre-design by running mini-plants is important. Industry relies on engineers to design the plant systems and the pilot program to provide definitive cost information.

8. Reagent Purity

- Many reagents are not 100% pure, and therefore the impurities of the manufacture can be a short-term problem in the plant due to formation of stable emulsions / precipitates / 3rd phases. These impurities, if shown to be present, should be removed by a wash, possibly a caustic wash, or an acidic wash. Ideally, the wash should be performed by the reagent manufacturer. In some similar reagents used for the same metal, and manufactured by different companies, the differences in the chemical performance and in the phase disengagement rates may be due to the presence of more impurities in one reagent than in the other.

- Some reagents are not accepted by a plant unless the reagent batch is first tested to be acceptable.

- Some as-received reagents may require contact with a solution in the plant to make them acceptable. The PLS has been used in some pilot plants for such a treatment. However the pre-treatment of solvents has not been usual in plant operations.

9) Reagent Degradation

- Degradation of some reagents can be high, as in the case of TBP, where mono- and dibutyl-phosphates are produced. These degradation products cause poor performance of the TPB extractant in the SX circuit, and unless the solvent is washed with caustic to remove the degraded products, the performance as regards the discrimination and phase disengagement becomes worse over time.

- Inorganic constituents can be highly degrading to the solvent. Nitrates in particular as well as nitrates + chlorides (aqua regia) have been shown to degrade the solvent (i.e. oximes in a Cu circuit.) Amines are readily degraded at an EMF above 600 mV.

- Isodecanol used as a modifier in many early uranium circuits was degrading at one plant to the extent that 10-15 gal of the modifier had to be added to the circuit every few days to maintain phase disengagement rates. No analytical procedure was available, so the determining factor for addition was a simple laboratory

phase separation test. Biodegradation of the alcohols to organic acids (through oxidation) leads to crud formation

- Other sources of degradation include concentrated acid in contact with the extractant, for example a copper oxime in contact with strong sulphuric acid will result in almost immediate reagent degradation. Also, strong acid should not be added directly to the organic phase in any part of the SX circuit.

- Solvent should not be stored in contact with acid, or stored in the protonated form, as this has been shown to cause degradation of amines.

- Algae and other natural organic compounds may be destroyed by use of biocides. These organic materials are common in tailings ponds, and if there is water recycle back to the plant, the organics can cause problems of poisoning on the solvent and producing cruds.

- Bio-leaching is used in the treatment of some ores, so that this is an area where biocides are not added of course, but certain of the metals or reagents may act as "biocides" and effectively decrease the microbe population in the raffinate for recycle. Re-inoculation may be required.

- In uranium operations, for example, although the object is to increase production, regulators are concerned with the environmental impact due to the plant. In the SX plants, where isodecanol may be the modifier used, degradation to the isodecanoic acid can be a problem in the plant due to solvent losses and crud formation, but also a soluble material in the effluent discharge. Tri-decanol is the recommended modifier for the U-sulphate-amine system and has been in use for perhaps 20 years. A few plants still use isodecanol. The tri-decanol is more stable to degradation by oxidation. Use of TOPO might be a consideration as a modifier, and it also acts as a synergist. However this system is also more difficult to strip

- Contaminants may speed up degradation. Clay treatment is used in many plants to remove "unknown" materials from solvents, thus enhancing phase separation rates for a short time period.

10. Decrease Entrainment in Plant Effluents

- Entrainment of organic in the recycle water can adversely impact the process as causing poor metallurgy and poor physical performance. Soluble losses vs. temperature are then of increased importance.

- Entrainment starts in the mixing stage, usually in the 1st stage and becomes worse by the end of the 2nd stage in a 2-stage primary-secondary mix circuit. Normally, the misting is worse in the primary mix stage.

- If pre-equilibration is required, as in the control of equilibrium pH in an alkylphosphorus acid system for Co-Ni separation, it is advisable to add the alkali directly to the organic phase. Otherwise local precipitation can occur. In one such plant, although the phase separation in the first stage of extraction was 35 seconds, the small amount of precipitate became more stable as an emulsion/crud, and by the 5th stage, the separation time was up to 10 minutes. That plant has now changed to pre-equilibration of the organic phase (the amount of alkali based in the amount of metals to be extracted) with the result that there is no further problem with high entrainment losses due to localized precipitates and stable emulsions/cruds formed.

- Need to design for operation based on the kinetics in the mix stage required for optimum mass transfer. This is particularly critical when high shear pump-mix design is used in mixer settlers.

- Many plants with the primary and secondary mix designs have shut down the secondary agitator without adversely affecting the mass transfer, but resulting in better phase separation rates and therefore decreased entrainment losses.

- Large mixer settler units require high power distribution and the use of two mixers (to increase residence time for mass transfer) also increases power consumption.

- Why not use in-line mixers where kinetics are suitable for mass transfer? Perhaps the reasons include
    - Unknown properties of design and scale-up,
    - Unknown pumping costs, and
    - Lack of published plant experience.

In one pilot plant operation, in-line mixers for uranium recovery from sulphate leach solutions showed 92% recovery in 10 seconds. At the low shear, mass transfer was achieved without a phase disengagement problem that occurs in conventional operating plants at high shear and mixing for 90-120 seconds and achieving perhaps only 88% U recovery. In addition, with the mixer settlers, phase separation time was longer and entrainment losses were higher. The in-line mixers are best run at plug flow, and at about 90% of flooding throughput. In-line mixers have had demonstrated success in the recovery of uranium from phosphoric acid using DEHPA-TOPO so that uranium becomes a by-product in the production of fertilizer.

In-line mixers have recently been successfully proven for the recovery of copper by a Koch-design contactor.

In-line mixers, with the low shear, result in excellent phase separation as a result of little or no dispersion band depth. Therefore the entrainment losses are low and the throughput per cross-sectional area is high compared to the mixer settlers.

- Columns will also result in low entrainment losses if operated correctly, particularly when using pulse columns. If the kinetics are too slow to consider in-line static mixers, then the longer time a column provides for mass transfer may be preferable.

- Precipitation of solids within a contactor can often be a problem, and the longer the time in the contactor the greater the opportunity for sedimentation to occur. Thus, the in-line mixer would be expected to have little or no chance for solids deposition.

- Columns (certain designs) and in-line mixers (certain designs) are capable of accepting solutions containing several 100's ppm suspended solids without producing a crud.

- Recovery of values from the leach slurry, where % solids are present, (solvent-in-pulp, SIP) has shown that in pilot plant operations using sieve-plate pulse columns, the solvent loss is by adsorption on specific mineral surfaces. In the case of uranium recovery with amines, the minerals pyrite/sericite/quartz were found to be the most adsorbent of the amine. Losses could be essentially eliminated when treating up to 55% slurry leach by first contacting the slurry with diluent. The molecular layer of diluent coating was sufficient to prevent the attraction of amine to the mineral surfaces. For the same extraction, using DEHPA, there was no "mineral attractive force" as in the amine system. Minimal solvent losses in all systems that have a tendency for crud formation are attained when the process is run organic continuous.

- Entrainment losses are affected by air in the process, through mixing, vortex formation, and the spill over launders. "Fish eggs/fish eyes" are formed and when these droplets break, "misting" occurs. The mist contains not only the organic constituents, but also the metal being recovered, such as Cu, U. Thus a very toxic situation is produced in addition to increased entrainment in the presence of air.

- Introduction of the mixed phases (in a mixer settler operation) into the dispersion band can decrease entrainment losses, and may also decrease misting as caused by air entrapment.

- Need to consider mixing / high shear / turbulence vs. additional pumping costs of in-line mixers, the questions are:
    - o Do we require a better design of mixer settlers, or
    - o Should the industry be committing more effort to the application of in-line mixers (or columns)?

- Improvements in the development of pump-mixers should be considered in the design of a particular application.

- What can be done in settlers for improvement? Require a good dispersion band to feed the mixed phases into. Use of FRP, stainless steel, PVC, Teflon, polypropylene-coated alternate plates or picket fences should be considered for application in order to decrease entrainment losses.

- Need to slow down the linear velocity to permit for more complete coalescence; also high linear velocity produces back flow along the walls of the settler. The rate of coalescence is proportional to the linear velocity.

- Inventory of the solvent and the flow pattern of organic are considerations in the operation for minimizing entrainment.

- Amphoteric compounds such as Zr, Hf, Mo, W, Nb, Ta, Si, Al, Bi etc have a tendency for fast extraction onto the solvent and are only released as saturation for that particular species is reached—usually in the strip circuit. Although many of these amphoteric compounds were undetected in the ore or the PLS, they accumulate in the solvent, to the extent that in U circuits for example, 10 % Zr or 35% Bi have been analysed in the crud. As these compounds accumulate on the solvent, the viscosity is adversely affected with the result that phase separation rates decrease and increasing entrainment losses occur.

- As crud accumulates in the settler, the mixed phases that are separating will form eddies that may travel in the reverse direction of the flow. Phase separation rates are therefore affected.

- Solvent losses are caused by solubility, entrainment, crud, degradation, misting, spillage and poor housekeeping. Recovery has been achieved by mixed media filters, and flotation (Jameson cell). Entrainment losses are difficult to predict, and may be related to the contactor design and energy input to the system.

- In-plant sampling and analyses can be difficult as regards entrainment losses.

- What is the value for solvent loss in an SX circuit? Is there a maximum or minimum design value? The total loss will depend on the organic concentration (in the solvent) and the operating conditions. Soluble loss is generally considered low relative to entrainment.

- What are the problems with measuring loss by entrainment and then what does one do with the information? There appears to be no resolution to this question. The losses with mixer settlers and columns can be low but there is room for improvement. A level of 30 ppm or less would be ideal to achieve. It may be difficult to make an improvement in operating practice to result in decreased entrainment losses due to the particular contactor design

- Recovery of entrained solvent by flotation, such as by the Jameson cell, has not been very successful to date. Flotation seems to remove the bulk of the entrained

organic, but it can be difficult to attain less than 30 ppm of entrained solvent. Flotation has also been used to treat the strip electrolyte, followed by carbon filtration or dual media filtration, prior to electrowinning. Flotation reduces the load on the subsequent carbon or dual media treatment. In the early Bluebird operation in the late 1960's, a bank of 45 Denver flotation cells were successful in the removal of considerable solvent prior to recycle of the raffinate to the heaps.

- Entrainment losses can also be related to the plant design relative to the operating practice.

- DEHPA losses in a centrifugal SX plant have been low in one rare earth circuit, and measured a total of 7 ppm by inventory after 7 years of operation.

- How much effort is required to improve the settler? Bateman, (and others) have made improvements in the reverse flow settler, and Outokumpu in their mixer design resulted in improvements in settler operation. Some plants in Australia and Chile have been using mesh bags containing cut-up poly pipe to assist coalescence. However, the practice has not been successful at all plants, so many have now removed the baskets due to the organic coating of the pipe which then ultimately results in poor coalescence.

- Broken glass, evenly spaced (a home-made remedy) appears to work better than systems available on the market (the members of the discussion group have problems with systems operations and equipment offered by various vendors).

- Why not make tanks (settlers) smaller and install a coalescer? The Goro project was reported to use coalescers. Electrostatic coalescers should be considered because of the improved separation efficiency, but there also could be the danger of fires. Electrostatic coalescers have been used in the oil industry with low fire incidence.

- Some companies have developed technology using electrostatics for coalescence enhancement. A refinery in Louisiana uses coalescers; however energy cost using such a system is not known.

11. 3rd Phase Formation

- A 3rd phase refers to the condition that results from instability in the solvent phase that causes the heavy reagent to separate from the lighter diluent. The reagent, being close to the S.G. of the aqueous phase, will be lost to the process raffinate.

- High concentrations of metal in the solvent may result in 3rd phases in some plants; need to operate at perhaps 15% less than solvent saturation. This has been the case with the use of the phosphinic acid in the separation of Co-Ni and also in systems that have potential hydrolysable compounds (usually amphoteric).

- Some circuits, such as U require a modifier (long chain alcohol) addition to prevent 3rd phase formation. The problem can also occur in the use of alkylphosphorus extractants at high loading, and where (TBP) modifier is required to maintain the metal-complex solubility in the organic phase.

- Chelating reagents already have a modifier in the reagent, and therefore the problem of 3rd phase formation is not really a problem,

- The presence of bacteria can attack the extractant, and therefore cause a 3rd phase. Bacteria will also attack the modifier.

- Strong acid in the presence of some solvent systems may cause a 3rd phase. This has been noted several times in uranium plants.

- A 3rd phase may take some time in the plant to completely form, and the problem may be indicated by a sudden severe loss in loading (high raffinates) which becomes worse over perhaps a few days or week, until no extraction is occurring at all. By that time, all the extractant has been lost and discharged with the raffinate.

- .The less ionized the aqueous solution, the more the tendency for 3rd phase formation.

- With recycle of reagents, there may be an accumulation of "organics" or degraded substances on the solvent phase. The effect is poor phase separation, and high entrainment losses of solvent. If the solvent is sufficiently fouled, a 3rd phase may result if the solvent is not kept clean.

12. Crud

- Many cruds have now been identified—solid state emulsions, packing at the weirs, at the interface, or on the bottom of settlers. The term crud was derived from a nuclear plant in Canada using SX, in which the description of the visual problem was "Chalk River Unidentified Deposit", which was shortened to C.R.U.D. The periods were removed to have the descriptive word crud. Most common constituents in cruds have been identified as Ca, Mg, Al, Si, Fe plus the metal being recovered by the SX process.

- Crud formation is the result of something upstream—not just the high shear in the mixing that can also contribute to crud formation. Amphoteric compounds which are easily hydrolysable are now known to be a problem of solvent poisoning and the ultimate cause of crud formation as these compounds come out of the organic phase as a precipitate in the aqueous phase. Of course Si has been blamed for crud formation for a long time, but all other amphoteric compounds can be as detrimental, and some worse.

- Bi has been found to be as high as 35% in a strip crud, while Zr was measured at 10% in several plants. Neither element was detected in the ore or the PLS. The amphoteric compounds also have very fast kinetics, and will often extract faster than the desired metal for recovery.

- The poisoning of the solvent with such as amphoteric compounds, and the resulting crud formation, means that frequent cleaning of the solvent is required to maintain a level of poison that does not adversely affect the SX process through precipitation/crud formation.

- Mg was found to be the accelerator to crud formation when in the presence of Ca, Al, Si, and Fe. No scientific reason has as yet been determined. However, in many plants processing laterites rich in Mg/Fe, there are large quantities of crud formed.

- Polymeric species (e.g. of Si, Zr, Mo etc) of an amphoteric are prone to forming gels and cruds. The formation of the colloids is due to the acidity at some place in the process, often during the leach stage when strong acid is available early in the leach.

- The presence of insects in the system can be a severe problem, and when in contact with strong acid as in the extraction, stripping and EW circuit, are attacked to form fulvic acids. These organic acids, together with those organic acids from a heap operation, humic acids, poison the solvent and subsequently contribute to poor plant performance as well as crud formation. The open EW plant, if well lighted at night, will attract many insects that result in the formation of considerable high molecular weight organic acids.

- Agitation at high shear can produce a crud even in the absence of any suspended solids. Mass transfer for metal recovery, without crud, may be attained at a considerably lower shear, but with the pump-mix agitator design, it is conducive to crud formation.

- Some operators claim that the presence of some crud actually assists in the phase separation and reduction in entrainment. Crud as well as sand have been introduced into the mixing tank in some operations to suppress crud formation! No scientific explanation has been given as yet.

- Columns with centrally-driven shafts, because of the axial mixing and back mixing, are prone to crud formation, similar but less amount compared to using a mixer settler. Pulse columns run organic continuous have shown the best performance. In one plant, the amount of crud generated in a week period by a pulse column was about the amount generated for a similar process in a mixer settler plant in 1- minute.

- In one Cu plant, 5-tonnes of crud were produced in a week before the problem (solids carry-over from extraction to strip) was corrected with the addition of a scrub stage.

- In-line mixers have been run successfully for extraction, scrubbing and stripping without any crud and phase separation problems. Koch has recently had a successful plant trial on a Cu circuit using an in-line mixer design.

- Crud treatment varies throughout the industry, and includes:
  - Allowing the crud /solvent to settle followed by recovery of the solvent by decantation
  - "Sucking" of the crud off the settler followed by a wash treatment of the crud and filtration to recover the solvent
  - Separation of solvent from solids by 3-phase centrifuge
  - Send to a special pond for gradual recovery
  - Send to tailings

Any solvent recovered from a pond will have been exposed to severe oxidation over time, so there may be considerable degraded products present. If these degraded products are not removed by a prior treatment, then recycling can cause problems in the plant

- Prevention of poisoning and crud formation may be accomplished by consideration of:
  - Diluent wash of the PLS (organic acids and some chelates)
  - Treatment (caustic wash) of a bleed solvent
  - Reduction in the shear in mixing (stable emulsions, misting, crud)
  - Covers over mixers and settlers (dust)
  - Minimize air entrainment to system (emulsions)
  - Improved picket fence design in settlers (materials of construction)
  - Minimize linear velocity down the settler (entrainment, misting)

13 Cross Contamination of Circuits

- Entrained solvent in the raffinate from the first of two SX circuits, if deposited to a pond where water is returned to the plant, will contaminate the 2nd SX circuit. Also, if the discharge from the 2nd plant is to the same pond, then contamination to the 1st plant also occurs. Both of these examples have occurred in at least one plant (Australia).

- Necessary to assure that the plants are completely separated in the plant design.

- Treatment of the raffinates by a diluent wash may be required to remove the entrainment

- Use of ion exchange treatment of the first raffinate may be a possibility in some plants to avoid cross-contamination.

14.   Solvent-In-Pulp (SIP) and Resin-in-Pulp (RIP) Systems

- The main advantages of using SIP are:
    - The elimination of the high capital and operating costs (approximately 50% of each for the mill operation) connected with the liquid-solids separation;
    - Recover the additional metal soluble values that are normally trapped in the washed leach residue, which can amount to 5% or more of the production.

- Each plant, because of the mineralogy differences as well as the extractant used, will be unique in the type of process used.

- Pulse columns and in-line mixers appear to offer potential for such a process.

- According to some reports, some SIP plants have been operating in China using sieve plate pulse columns.

- As to the future of SIP, although work started on the possibility almost 50 years ago, the time for implementation may be very soon, particularly now that column and in-line mixer technologies are rapidly gaining acceptance as an alternative to mixer settlers.

- The use of resin-in-pulp (RIP) requires the flotation recovery of the resin

15.   Measurements of Plant Performance

- Humic or fulvic acids, if present, are quickly extracted by not only the reagent but also the diluent. These extracted organic acids are capable of extraction of many metals. For example, Fe is not supposed to extract with a tertiary amine, but in the presence of the organic acids, up to 25 g Fe/L have been found in the strip solution in an amine-sulphate uranium system.

- Plants that require a regeneration as well as a protonation stage (e.g. uranium-amine circuits) should be using dedicated mixer settlers for each stage. There is a tendency in many operations to run the stages intermittently and only using a single mixer settler that is shared. These SX stages should be continuous, not intermittent.

- It is important to run the plant, almost from the start-up, at design capacity. Anything less will mean excessive mix time (longer than required for mass transfer based on the kinetics) under high shear that produces smaller and smaller droplets resulting in poor phase separation. An example of one Cu plant which started up at about 60 % throughput, gradually decreased to 28% and had to shut-down. However when re-started at 92%, the plant operated well and the throughput was subsequently increased gradually over a few months period to

reach 130% design. But the exercise had cost the company 3 years of high operating costs and reduced revenue!

- Effect of interfacial area - know the interfacial distribution reaction kinetics and mass transfer, that may be predicted from modeling. The model may be accurate for idealized systems. Accumulated data are now available for modeling of Cu circuits, but are not suitable for other systems, such as Zn for example. The model is not based on fundamental data. The effect of interfacial area is not used. Without such data, the design of the contactor may not be reliable.

- Copper plants in Chile and Australia (and elsewhere) measure interfacial tension relative to mass transfer (loading) in order to follow the plant performance. The frequency of measurements differ from plant to plant.

- On a routine basis (weekly), measure and compare the loading, discrimination over impurities in the solvent, and the product purity so as to recognize if a serious plant problem is slowly developing.

- A Fisher Tensormatic 20 is commonly used for laboratory surface tension measurements.

- Characterization of the solvent in the plant, before and after stripping is important, and will determine the volume of bleed solvent that must be sent for treatment. Monitoring of the surface tension (a characterization test) can be a guide as to deterioration in plant performance.

- Degradation of organics, to perhaps carboxylic acids, will adversely affect plant solvent performance, resulting in decreased loading, poor discrimination, high raffinates, and poor phase disengagement. These factors are all indicators of solvent poisoning.

- A bleed stream for treatment, if using a caustic treatment process, must be considered as to cost/benefits. Caustic consumption should be optimized by adequate design of systems and control philosophy.

- On-line instrumentation costs must be considered in the organic evaluation on a regular basis. Over a period of about 3 months there may be a gradual build-up of impurities (from the aqueous and solvent degradation). Hence the need to determine whether the solvent needs replacing or partial replacement due to a contaminant that has been extracted and not stripped. The contaminant may require being removed by precipitation by such as lime addition. The surface tension measurements are important. The expenditure on instrumentation may save some expense in solvent treatment costs. It is amazing that instrumentation costs have to be "justified" as against the cost of organic regeneration

- Data on gallium extraction circuits have identified various elements that load on the organic and are difficult to remove (poisons). Organic is replaced at high cost without having tested the feedstocks for "poisons". It is possible that continuous testing and monitoring of the feedstock may be used to optimize an operating cost.

- Viscosity and density should be measured on a shift basis. Well-run plants are making such measurements using very simple techniques (such as recording the time to drain from a 60 mL pipette, correlated to change or relative change in viscosity).

- The key indicators, as noted earlier, include routine tests performed on a regular basis to determine loading, phase disengagement, interfacial tension.

- Viscosity measurements should be made on stripped and non-stripped solvents and compared to phase disengagement measurements. Amphoteric compounds have been shown to be particularly poisonous to solvent systems and can appear as a crud in the stripping circuit in the best cases, but may also remain on the stripped solvent and require removal by a caustic treatment of the solvent.

- Over-design problems – can make or break the process. Often, the plant is over-designed by a factor of 2. How much over-design can be tolerated and how much will the design impact on the cost and efficiency of the SX circuit?

- There is a need for better measurements for design. The designer should also consider phase disengagement. It was noted that in addition to the mixer there must be an emphasis on the settler design. With an improved mixer design and fine droplet size the design of the settler may be affected.

- There are some data from operating plants using mixer settlers, but very little from column plants as regards poisons.

- The operation of a pilot utilizing a mixer settler may be used to determine the suitability of columns for a specific application.

- Diluents are not easily oxidized, although some components may be. There is the potential oxidation in the presence of metals of higher valencies, i.e. V^{5+}. There may be the need to monitor for carboxylic acid formation if oxidation of the diluent is suspected.

16. Novel Processes

Discussion on the use of novel techniques was also limited. Novel SX systems and associated technologies have been developed for non-traditional systems, specifically for low concentration of metals in the pregnant solutions.

- Application of a novel process means a good understanding of the process and the practical aspects:
    - May be difficult to attain as good separations as in SX;
    - Systems can include colloidal, nanoparticles, magnetic field coatings

- Use of SX for waste treatment

17. Metals Extraction from Dilute Solution.

- Use of ion exchange for removal of metal ions (using static mixed beds) has been developed for acid mine drainage solutions.

Use of SX for treatment of industrial wastewater would be considered more efficient than IX with respect to pumping costs, mass transfer, large resin bed requirements, etc. It is estimated for some applications (flow not defined) that about 45 large resin beds (5 meter diameter and about 10 meter high) are required to treat wastewater effluents. Use of SX is expected to be more viable than IX. The solvent extraction process is more easily controlled and possesses better selectivity as compared to ion exchange.

18. Safety Issues

A group discussion on recent fires reported in SX plants identified the need to review materials of construction, electrostatic/grounding systems, plant layouts and fire abatement systems. Both design and operating measures to prevent fire are very critical to the future of the solvent extraction industry. With such risk and the potential for a huge loss of revenue, it is possible that companies may turn to other technologies. Further analyses of the cause for fire and recommendations for design and operating standards should be based on a documented incident report (to be published at Hydro-Sulfides 2004, April 2004, Santiago, Chile). The need to establish a committee to address design and operating guidelines for solvent extraction plants was identified during the group discussion. Some generalized aspects of plant safety that were discussed follow.

- In most cases the selection of materials may be critical to the safe operation of the plant. For example, a) electrical wiring may have PVC coatings for insulators and solvent may dissolve PVC and expose the wire; and b) fire spread using high density polyethylene (HDPE) tanks or piping.

- Serious consideration in safety must include electrostatic generation, dissipation and/or elimination of sparks.

- Antistatic reagents have a detrimental effect on phase disengagement.

- High shear mixing and pumping large volumes through pipes, if not properly grounded, will cause a charge to be generated.

- A high flash point diluent is required.

- Within the SX plant, there are a significant number of electric motors. It is common to use an explosion proof motor on the mixer and pumps, but it is noted that sparks can be generated from such motors. Further review of motor selection and measures to prevent spark generation is required.

- Misting that occurs in many mixer settler plants have a potential for static electricity formation.

- Earthing of solvent storage tanks is required.

- Synthetic clothing, walkways with synthetic coverings, etc are potential hazards as regards static generation.

- The safety plan should include a firewall in order to protect individuals.

- Ground and bund areas.

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