EXPERIENCE WITH CRYSTALLISATION AS SUSTAINABLE, ZERO-WASTE TECHNOLOGY FOR TREATMENT OF WASTEWATER

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ABSTRACT

Precipitation is a frequently applied physical/chemical treatment process for removal of metals and anions like sulphate, fluoride and phosphates from process and wastewater. Crystallization in fluid-bed crystallizers, so-called Crystalactor®, is a versatile alternative to these conventional processes. The zero-waste and cost-effectiveness characteristics of the proven crystallization technology make it a truly sustainable alternative technology offering mines and metallurgical industry opportunities to combine water treatment and/or raw product recovery with significant economic and environmental benefits.

1. INTRODUCTION

Mine water treatment has often been associated with significant capital cost, operating cost, and an open ended liability for mine and process facility owners. The search for the 'silver bullet' in treatment technologies continues, but the hard reality of chemistry and physics suggests that tailored application of existing proven technologies within existing water flowsheets is the way to go.

Best of breed trials and combinations are offered to industry on both a turnkey (normally resulting in costly plant with on-going environmental liability still quite high and being left with the owner) and speculative investment basis (where progress is impended through difficulty in obtaining sufficient funds and resources). However, the very real and looming water shortage in South Africa, coupled with the rapidly rising cost of obtaining and supplying raw water for new operations is providing impetus to the development of sustainable water treatment solutions-that is, solutions which offer real potential to be cash positive both during and after normal mine operation. This paper provides an insight to potential contribution of the well proven Crystalactor technology to this objective.

Precipitation is a frequently applied physical/chemical treatment process for removal of metals and anions like sulphate, fluoride and phosphates from process and wastewater. Precipitation is also widely used within the mining and metallurgical industry for e.g. metal recovery, AMD-treatment and water softening. In general, the sludge produced in such precipitation units has a poor quality, disabling reuse of the sludge. As a consequence, the waste sludge, that after dewatering often still comprises 60-85% water, has to be disposed of at high costs and remains an environmental liability. Also the required footprint for a conventional precipitation process is high since four separate process steps are involved: coagulation, flocculation, sludge/water separation plus sludge de-watering, while especially the sludge/water separation in settlers requires high hydraulic residence times.

An advanced alternative for conventional precipitation is crystallization in fluid-bed type crystallizers. This technology has been developed originally by DHV and the Water Works of Amsterdam in the seventies as a cost-effective technology for the central softening of drinking water. The same, so-called Crystalactor® technology1 was in the eighties and nineties further introduced into the international water treatment market for the recovery of heavy metals, phosphates and fluoride. Currently numerous units, with flow capacity ranging from 10 CMD up to 450 MLD, are in operation for both industrial and domestic water treatment. More recently, this zero-waste technology has also been recognized by the mining and metallurgical sector as a cost-effective and sustainable proven technology for use in treatment schemes such as extraction, mine service water treatment, acid mine drainage (AMD), ground water (fissure water) and wastewater.

The technology is well proven in a variety of applications and is now fully backed in Southern Africa from application selection through to full plant engineering and operation by DHV companies and its partners.

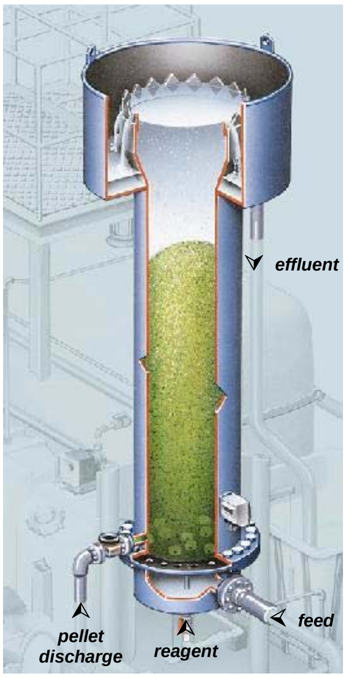
[1] The Crystalactor® is the registered trade mark for fluid-bed crystallizer systems developed by DHV for water treatment

2. TECHNOLOGY DESCRIPTION

Actually, the chemistry of the process is comparable to the conventional precipitation. By dosing a suitable reagent to the water (e.g. lime, calcium chloride, soda, caustic soda), the solubility of the target component is exceeded and subsequently it is transformed from the aqueous solution into solid crystal material. The primary difference with conventional precipitation is, that in the crystallization process the transformation is controlled accurately and that pellets with a typical size of approx. 1 mm are produced instead of fine dispersed, microscopic sludge particles.

Principle

The Crystalactor® is a cylindrical reactor, partially filled with a suitable seed material like sand or minerals. The water is pumped in an upward direction, maintaining the pellet bed in a fluidized state. In order to crystallize the target component on the pellet bed, a driving force is created by a reagent dosage and sometimes also pH-adjustment. By selecting the appropriate process conditions, co-crystallization of impurities is minimized and high-purity crystals are obtained.



Picture 1. Principle of Fluidized Bed Crystallizer

The pellets grow and move towards the reactor bottom. At regular intervals, a quantity of the largest fluidised pellets is discharged at full operation from the reactor and fresh seed material is added. After atmospheric drying, readily handled and virtually water-free pellets are obtained.

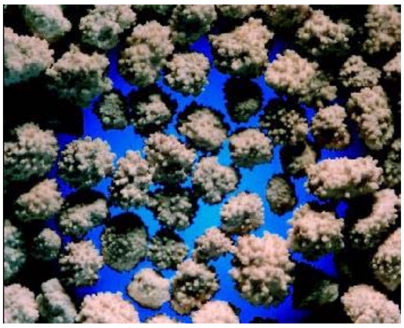
No Residual Waste

A major advantage of the process is its ability to produce highly pure, nearly dry pellets. Table 1 shows the typically characteristics of the pellets in comparison with precipitation sludge.

Due to their excellent composition, the pellets are normally recycled or reused in other plants, resulting in no residual waste for disposal. In the rare event that pellets have to be disposed of by other means, the advantage of low-volume secondary waste production still remains: water-free pellets, not bulky sludge.

Table 1. comparison of characteristics of by-product

Parameter	crystallization in pellet reactor	Conventional precipitation
morphology	round pellets 0.8 - 1.0 mm	Sludge
water content	1 - 5 %	60 - 85 % (after mechanical dewatering
seed material content	< 5 %	-



Picture 2. compact, reusable pellets (calcium fluoride, shown magnified)

Compact

The four process steps found in conventional precipitation processes – coagulation, flocculation, sludge/water separation and dewatering – are combined into one by the fluidized bed crystallization. Furthermore high surface loadings, typically in the range of 40-120 $m^3/m^2/h$, are applied and subsequently the crystallization unit is compact.

Applications

The oldest application of the crystallization technology concerns the softening of drinking and process water. Since the seventies major drinking water works and industries successfully apply the technology for efficient water softening. Based on this experience the technology was further developed for metal, phosphate and fluoride recovery applications.

In principle almost all heavy metals, metalloids and anions can be removed from all kind of water types by crystallization as long as the solubility of the produced salt pellets is low and the metal or anions crystallizes quickly into a stable crystal lattice.

As shown in table 2, there is extensive experience and the number of applications continues to grow. Metals are generally removed as hydroxide, carbonate or sulphide compounds and in some cases it has proved to be attractive to form metal phosphates. Anions like fluoride and phosphates are usually removed as calcium salts. Occasionally it is more desirable to form complex salts. For example, phosphate can be removed as NH4MgPO4 while simultaneously reducing the wastewater nitrogen content.

Table 2. Periodical system showing crystallization experience

1 H																	2 He
3 Li	4 Be					successfully recovered						5 B	6 CO3	7 NH4	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 PO4	16 SO4	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57/71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89/103 Ac-Lr	104 Rf-Ku	105 Ha-Ns	106 Unh	107 Uns	108 Uno	109 Une									

Picture 3. Crystalactor for softening of drinking water, Municipal Drinking Water Company of Amsterdam, The Netherlands. Capacity: 8,500 m3/h

Picture 4. Crystalactor for nickel and aluminium recovery from spent catalysts

3. APPLICATIONS IN MINING & METALLURGICAL INDUSTRIES

Given the recent challenges in managing aqueous emissions from mining and metallurgical industries, plus the word-wide trend for more sustainable solutions, the zero-waste and cost-effectiveness characteristics of the Crystalactor technology make it an interesting and useful element for treatment schemes in these industries. Whereas several applications were already mentioned, some specific applications examples in mine & metallurgical industries are presented below.

Water Softening/Desalination

In general the technology has proven to be very cost-effective wherever large water volumes have to been softened or desalted. As a part of the overall flow scheme development for treating AMD and underground fissure water at Gold Fields Driefontein mine into drinking water and saleable products, Watercare Mining is applying the technology as a pre-treatment step prior to more extensive demineralisation in ion exchangers. The flow-scheme has been piloted since April 2009 and is showing good results. The calcium hardness is reduced from typically 76 ppm Ca to the desired level of 36 ppm Ca and the efficiency of the crystallization conversion is close to 99%. An interesting feature is that the calcium carbonate pellets produced in the unit can be calcined into lime. By doing so, the process does not only produces its own reagent (lime is used for the softening process) but also produces a significant amount of excess lime that can be used elsewhere on the mine or packaged as saleable product. The overall reaction equation is as follows:

$$Ca^{2+} + 2\ HCO_3^- + Ca(OH)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O$$
$$\underline{2\ CaCO_3 + 2\ H_2O \rightarrow 2\ Ca(OH)_2 + 2\ CO_2 \qquad +}$$
$$Ca^{2+} + 2\ HCO_3^- \rightarrow Ca(OH)_2 + 2\ CO_2$$

Table 3. estimated preliminary operating costs for hardness reduction at Gold Fields (price level June 2009, estimate based on pre-feasibility data)

Operation & Maintenance	R 0.05 / m^3
Chemicals	R 0.12 / m^3
Power	R 0.06 / m^3
Pellet utilization	- R 0.21 / m^3
Total	R 0.02 / m^3

Picture 5. Crystalactor pilot plant at Gold Fields Driefontein's mine

In many water recycling and desalination schemes, reverse-osmosis (RO) has become a well recognised and used technology. Early applications of the Crystalactor occurred in the eighties for large desalination plants in the Middle-East, where the technology was used to reduce the water hardness prior to the RO enabling a higher concentration factor and thus minimizing water losses.

More recently, the handling and disposal of brine discharges from in-land desalination plants became a challenge. Following flow schemes have been developed to meet such challenges:

a) Crystallization for removal of calcium, barium and silicates from the RO-concentrate to enable treatment in a second RO-stage (figure 1)
b) Crystallization to transfer RO-concentrate into product water for e.g. cooling water make-up

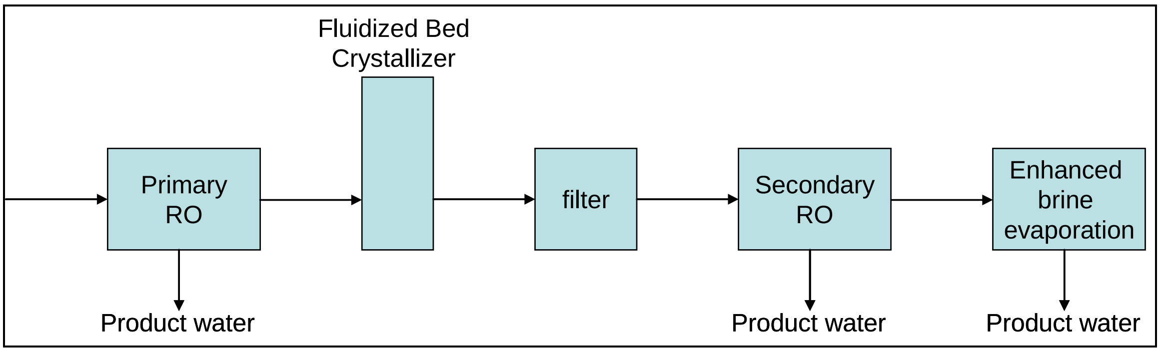


Figure 1. Example of a zero-waste desalination scheme for in-land desalination

Heavy Metal Recovery

One of the existing key applications of the Crystalactor is recovery of precious and other metals from process and wastewater. While historic applications have been predominantly driven by the need to purify waste streams and to prevent further pollution in Europe, the dire shortage of water, coupled with a vibrant mining and metallurgical industry in South Africa has provided impetus to extending applications on a direct business return basis as well. For example, the technology might be useful for recovery of metals from tailing dams. In recent work for a copper mine, economic viability was proven in recovering dissolved copper from the tailing dams and historical wastewater storages dams. Also, various scheme developments for Asian mines show that the Crystalactor is an interesting unit operation to combine emission reduction with metal recovery. Table 4, shows a typical example of the economic benefits of reclaiming valuable metals from wastewater rather than to transfer them into waste. In many cases, the overall operating costs for such "environmental" applications are outbalanced by the value of the recovered metal pellets and the saving on waste disposal.

Table 4. typical operating costs for nickel recovery from wastewater (100 m3/h, 150 ppm Ni)

Cost item		
Maintenance		€ 15,000
Labor		€ 5,000
Electricity	200 MWh	€ 14,000
Seed material	12 ton	€ 2,000
Saving on waste disposal	490 ton	€ - 74,000
Value pellets	246 ton	€ - 320,000
Reagent		€ 148,000
Total		**€ - 210,000**

Fluoride and Phosphates Recovery

Wherever aqueous fluoride emissions occur in metallurgical or mining industry, the Crystalactor seems to have potential attractive application. For example, already since the early 1990's, the Crystalactor has been used at a zinc refinery to extract fluoride from a closed-loop water system. Also is the technology used to recover phosphate from for example municipal sewage.

In general, by-products of the process can be easily used as raw material for the fluor and phosphor industry, and in principle, phosphate pellets could be reused directly as fertilizer as well. Table 5 shows typical operation costs for fluoride recovery (15 m3/h, 700 ppm F) compared to conventional fluoride removal by precipitation.

Table 5. comparison of annual operating costs for typical fluoride recovery (15 m3/h, 700 ppm F)

Cost item	Conventional precipitation		Pellet reactor	
Maintenance		US$ 6,000		US$ 6,000
Labor	2 h/day	US$ 10,000	1 h/day	US$ 5,000
Electricity	17.5 MWh	US$ 2,000	52 MWh	US$ 6,000
Seed material			10 ton	US$ 1,000
Disposal wastes	766 ton	US$ 230,000		
Disposal pellets			220 ton	US$ - 40,000
Reagent	220 ton	US$ 66,000		US$ 66,000
Floc aid	1.3 ton	US$ 7,000		
Total		**US$ 321,000**		**US$ 44,000**

Sulphate Removal

The technology has been applied successfully on pilot scale to remove sulphate from wastewater by crystallization of either gypsum or ettringite. For treatment of AMD, a combination of biological sulphate removal and Crystalactor seems synergetic: sulphides produced during biological reduction of sulphates can be used to crystallize metal sulphides.

4. CONCLUSIONS

Crystallization in the Crystalactor® pellet reactor technology is a versatile and proven alternative to conventional precipitation-sedimentation-filtration processes for softening, metal recovery and fluoride/phosphate/sulphate removal. The zero-waste and cost-effectiveness characteristics of this technology make it a truly sustainable technology. It offers mines and metallurgical industry many opportunities to combine water treatment and/or raw product recovery with significant economic and environmental benefits.

Water treatment is fast entering a phase of business imperative. Intelligent application of proven technologies in better thought-through water balances provide the opportunity to turn what was previously a business overhead into a cash positive and sustainable solution.