Treatment of high-level arsenic-containing wastewater by fluidized bed crystallization process

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Abstract: Gallium arsenide technology has been widely applied in the communication and optical electronics industries. The process of chip manufacturing produces a stream of wastewater unique in its low flow rate and high arsenic concentration. Fluidized bed crystallization (FBC) technology combines the advantages of a fluidized bed reactor and crystallization. It is highly efficient with low capital and operational costs, while producing no sludge. The waste from the FBC is small in volume, high in crystal purity and recyclable. Jar tests were first performed to evaluate the precipitation of arsenic sulfide. Then a lab-scale fluidized bed reactor was applied to screen critical operational parameters and the process was optimized to meet the wastewater discharge standard. The results obtained in this study confirmed that the FBC process is capable of treating wastewater containing high concentrations of arsenic, reducing the concentration to $\mu g\,L^{-1}$ levels. Sulfide dosage and operating pH are the two most significant parameters determining the residual arsenic concentration of the effluent, with optimum conditions of pH = 2 and S/As = 2.2 to meet the local discharge limit.
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INTRODUCTION

Arsenic normally occurs at trace levels, as a result of rock dissociation, pesticide manufacture and gold mining.[1] Its toxicity gives rise to environmental concerns and so stringent discharge limits are applied to industrial wastewaters. Due to the fact that the mobility of electrons in gallium arsenide is higher than in a silicon device, gallium arsenide technology has been widely employed in communication and optical electronics applications. In the manufacture of light emitting diodes (LEDs), the As pollutants discharged from the Hsinchu Science-based Industrial Park (HSIP) originate from two sources: soluble As generated from the chemical vapour deposition (CVD) of AsH_3, and a solid residue from chemical mechanical polishing (CMP) of the final product. The former effluent was the focus of this study. The target wastewater is unique in its low flow rate and high As concentration mostly as arsenate. One typical LED fabrication process in the HSIP produced a wastewater containing $500-2000\,mg\text{-}As\,L^{-1}$ at $10-100\,m^3\,day^{-1}$. The pH of the wastewater was generally between 2 and 4.

Arsenic can be removed by chemical precipitation, chemical coagulation, adsorption and ion exchange, membrane filtration and activated alumina adsorption.[2] Bothe and Brown[3] have proven that lime adsorption is effective in reducing the mobility of dissolved As by forming precipitates of $Ca_4(OH)_2(AsO_4)_2.4H_2O$, $Ca_5(AsO_4)_3.OH$ and $Ca_3(AsO_4)_2.11/3H_2O$. A variety of metals, such as Ag, Ca, Mg, Mn, Cd, Fe, Al, S, Cu, Cr, Ba, and Pb, can react with As to form sparingly soluble salts.[4] Among these metals, Ca, Mg, S and Fe are most commonly used. Since $FeAsO_4$ only forms at extremely low pH, and Mg is more expensive than Ca, Ca and S are most often used for As removal. A previous study in our laboratory has shown that satisfactory removal of As by precipitation as calcium arsenate can be achieved at a pH greater than 11. Arsenic is also rapidly and strongly sorbed to sulfide minerals, in particular with sulfide minerals.[5] Veeken[6] reported that sulfide can reduce the mobility of dissolved As by means of chemical precipitation. He suggested that the two major As–S phases from hydrothermal solutions at temperatures below 300 °C are orpiment (As_2S_3) and realgar (AsS). Ferguson and Garvis[5] have also shown that As–S are formed at pH < 5 mostly in the form of AsS and As_2S_3. Until now, most LED factories in the HSIP have treated As-containing wastewater by chemical precipitation. However, the effluent from the process seldom meets the discharge limit and in addition, large amounts of sludge are generated because of the addition of precipitating agents.

Fluidized bed crystallization (FBC) was first developed for water treatment in the 1970s. DHV Water Treatment Engineering Consultants (Netherlands) initially applied this technology for drinking water

softening.[7] FBC technology has advantages over conventional processes in that several individual units can be combined into one column reactor. In contrast to chemical precipitation, FBC provides a large surface area for reaction, thereby requiring less space than the conventional coagulation/sedimentation method. It also uses less chemicals and produces less waste. Fluidized bed reactors have been applied extensively to various wastewaters containing impurities such as Ca, F, Ni, Cu, N, P, Zn.[8–11] The end product from the FBC consists of high-purity crystals of arsenic sulfide that can be recovered and reused in the manufacturing of paints, dyes and pharmaceutical products, a more economical approach than the conventional one.[8] In their study of heavy metal removal by FBC, Lee *et al.*[8] discovered that the pollutant removal and crystallization efficiency were affected by the choice of support, operating time, upflow velocity, pollutant loading per unit area per hour, metal dosage, pH, and pollutant concentration. The following were the most influential parameters: S/As molar ratio; As loading; pH, and feed As concentration.

This paper presents an innovative approach using FBC to immobilize As from wastewater containing a high concentration of As. The most critical operational parameters were screened by fractional factorial design and optimized using a Response Surface Methodology (RSM) coupled with Central Composite Design (CCD). The crystallization efficiency for the operation was also calculated.

EXPERIMENTAL
Materials and methods
Synthetic As wastewater
The wastewater was collected from a LED processing plant in the HSIP. It was characterized and served as a reference for preparing a synthetic wastewater. The As concentration varied between 479 and 1050 mg-As L^{-1} with pH close to neutral. The wastewater was gray to black in colour depending upon the concentration of the GaAs slurry. Synthetic As wastewater was prepared to simulate the LED wastewater by dissolving analytical grade Na_2AsO_4 in deionized water.

Jar tests for chemical precipitation were performed on the synthetic wastewater to evaluate As removal by precipitation of arsenic sulfide. The mixing device (PB-700 Jar tester, Phipps & Bird Inc., Richmond, VA, USA) consisted of a square acrylic vessel (11.5 × 11.5 × 21 cm). Mixing was provided by a 76 mm × 25 mm flat rectangular blade centrally located in the vessel driven via a thin spindle by a motor with speed adjustable from 10 to 300 rpm. Chemicals were injected just above the liquid surface. Following the work of Cornwell and Bishop,[12] the velocity gradient consisted of mixing for 1 min at a rotational speed of 200 rpm ($g = 350 s^{-1}$). After settling for 10 min the suspension was filtered through a 0.45 μm filter paper and the residual As concentration of the supernatant was measured by inductively coupled plasma-atomic
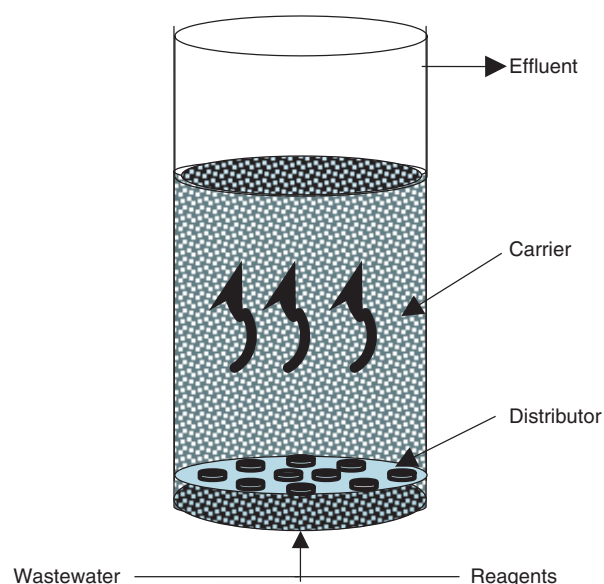

Figure 1. Fluidized bed reactor (FBC).

emission spectrometer (ICP-AES, Jobin-Yvon, JY-36, Longjumeau, France).

A 0.66 L (diameter 2 cm × 185 cm high) fluidized bed reactor (FBR) (Fig. 1), was used, containing a carrier, silica sand (about 400 g). Air was supplied from the bottom of the reactor while the distributor provided a uniform supply of air and wastewater. Sodium sulfide (Na_2S), sodium arsenite ($NaAsO_2$) and the As-containing wastewater were fed continuously into the reactor from the bottom of the column. The pH of the FBR was controlled by the addition of $NaClO_4$.

The metastable region of arsenic sulfide was determined using the method suggested by Tai *et al.*[13] to determine the concentration boundary of the reagent for primary nucleation. For the $NaAsO_2$–Na_2S system, Na_2S and $NaAsO_2$ were mixed in equal molar concentrations. Each solution was adjusted to pH 3.0 by adding HCl and was stirred at constant speed for 2 min. After standing for 120 min, a change in the solution from clear to turbid, indicating primary nucleation, was observed. The critical pH of the clear solution was recorded to plot the pAs and pS relationship, and the metastable region was located.

Takushi experimental design. Lee *et al.*[8] indicated that As removal efficiency depended on variables such as S/As molar ratio, As loading, pH, and As feed concentration. The Takushi experimental design was adopted to identify the key variables. The main effects and interaction effects were calculated using the statistical software ANOVA.

Central composite design. After the key variables for As removal were determined, CCD and RSM were used to determine the experimental conditions of the FBC to produce the desired residual as concentration and crystallization efficiency.

RESULTS AND DISCUSSION
Arsenic sulfide precipitation of the As wastewater

Jar tests were performed on the synthetic wastewater to evaluate As removal by precipitation of arsenic sulfide. The effect of operating pH was studied by measuring the residual dissolved As at an initial As concentration of $1048\,mg\,L^{-1}$, with the S/As ratio maintained at 1.5. More As precipitated at lower pH values (Fig. 2), and at pH 3 the residual As concentration was only $23.41\,mg\,L^{-1}$. The effect of S/As ratio on residual dissolved As was studied using the same initial As concentration, maintaining the pH at 3. Figure 3 shows that although increasing the S/As molar ratio increased the precipitation of As, no significant difference was shown over the range S/As = 1.5–3.5, possibly because the excess sulfide formed hydrogen sulfide $(H_2S_{(g)})$ instead of arsenic sulfide at such a low pH. In this experiment, the dissolved As concentration did not reach the theoretical equilibrium As concentration of arsenic sulfide, namely, $0.123\,mg\,L^{-1}$, as predicted by Dean.[4]

The jar test was performed at pH 4 ± 0.2 without any control on oxidation reduction potential (ORP). Under these conditions sulfide escaped the system as H_2S leaving a constant level of dissolved As in solution.
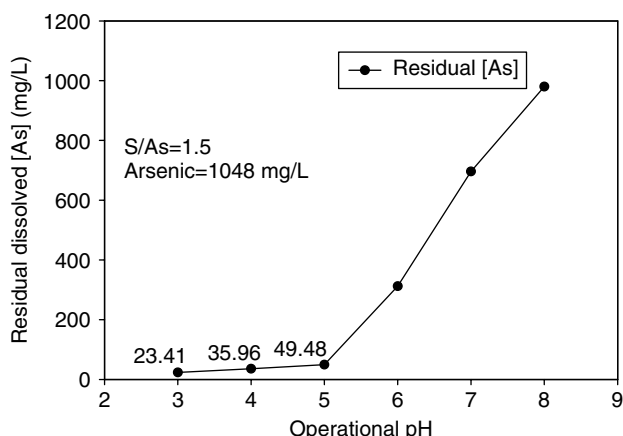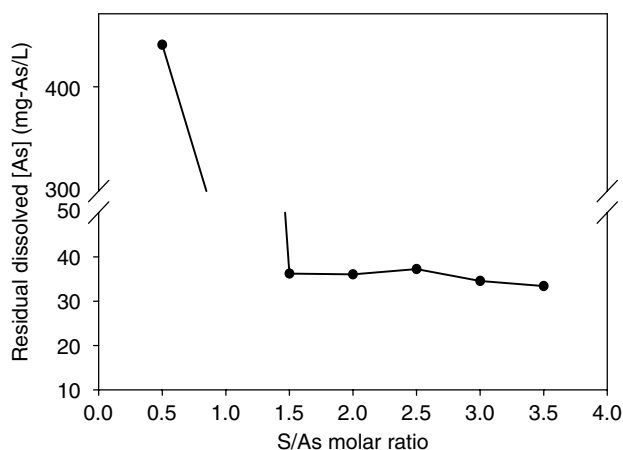
By controlling the ORP between 0 and $-400\,mV$, most As would react with sulfide to form As_2S_3 and AsS, to remove virtually all the As. Another source of dissolved As was the arsenic trisulfide precipitate flocs, which were smaller than $0.45\,\mu m$ and so remained in the filtrate, as shown by the yellow colour of the supernatant liquid.

Metastable region definition by arsenic trisulfide

The growth of arsenic sulfide crystals was illustrated using sodium arsenite $(NaAsO_2)$ and sodium sulfide (Na_2S) (Fig. 4). The metastable region was determined using the pH-stat method with the total As concentration between 10 and $5000\,mg\,L^{-1}$ at pH 3.0 and $25\,°C \pm 1\,°C$ In this figure Curve 1 is the saturation curve, and Curve 2 the lower boundary for primary nucleation. The metastable region for arsenic sulfide is between these curves, and denotes the range for crystallization. The ratio of crystallization and precipitation could be estimated from the sulfide ion concentration. For example, the concentrations of As and sulfide ion for primary nucleation at S/As = 1.5 are determined as p[As] = 1.88 ($988\,mg\text{-}As\,L^{-1}$) and p[S] = 2.81 ($50\,mg\text{-}S\,L^{-1}$). Under such conditions, $988\,mg\text{-}As\,L^{-1}$ can be removed as a crystal if the initial sulfide concentration was $50\,mg\,L^{-1}$. The results showed that the higher the S/As molar ratio, the lower the crystallization ratio. The percentage of crystallization can be enhanced by controlling the pH, feed As and sulfide concentrations in the FBR. Therefore, in addition to being maintained at an appropriate pH, the reactor must be kept at low super-saturation to produce a metal salt with low solubility in a stable crystalline state.

Screening of operational parameters

Fractional factorial design was used to screen the key variables by regression analysis with reduced experimental runs.[14] The experimental design allowed the influence of each process variable to be observed at a variety of levels, as well as investigating interactions between the variables.
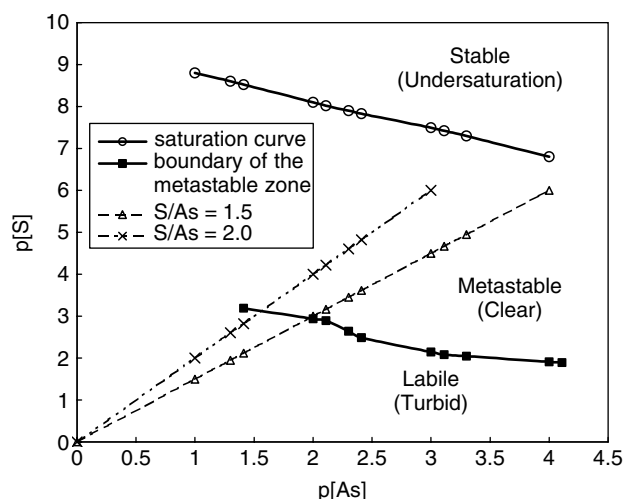

Figure 2. Effect of operational pH on residual dissolved As.

Figure 3. Effect of S/As molar ratio on residual dissolved As.

Figure 4. Metastable region for arsenic trisulfide.

Optimization of the treatment of the As wastewater was achieved by evaluated the effects of S/As molar ratio, As loading, pH, and As feed concentration. Table 1 lists the design factors and levels for these experiments. The chosen range and level of pH was based on the results of the jar tests on arsenic trisulfide formation (Fig. 2). The As feed concentration covered the concentration range of the real LED wastewater (200–1000 mg L^{-1}).

The fractional design matrix and the experimental results on residual As concentration are listed in Table 2. The two most influential variables were selected based on the major effects and the interactive effects of these four factors on the residual As concentration of the effluent. The 'effect' of a factor is defined as the change in response to the factor. The major effect for each variable is the difference between three averages. Figures 5 and 6 show the responses of residual As concentrations to different factor/levels with the larger the response, the larger the contribution of the factor. For residual dissolved As concentration, Fig. 5, the S/As ratio and pH were the two most important variables, both having positive effects on As removal. The effects of As loading and As feed concentration were relatively insignificant because the residual As concentration is limited by the solubility product. The response analysis for total As, Fig. 6, indicated that pH was the most influential variable. It was observed that during the operation, the column became clearer while the silica sand carrier turned yellow. For operations at lower pH values, a much clearer column was detected and the carrier changed to orange colour, indicating a denser level of crystals.

Optimization of FBC operation by CSM

After the two most influential variables (S/As and pH) were selected from the fractional factorial design, the condition of the fluidized bed was optimized using RSM[15] coupled with CCD. The experimental conditions were similar to the fractional factorial design except that the As feed concentration and As loading were maintained at 600 mg-As L^{-1} and 0.6 kg-As m^{-2} h^{-1}, respectively. Ten batch tests of the two-factor CCD covering operating pH from 1.3 to 2.7 and S/As molar ratios from 1.7 to 2.3 were performed. The operational results, analyzed using the MATLAB software (MathWorks Inc., Taiwan), are shown in Fig. 7.

Two sets of information are provided by Fig. 7. Parallel lines running from upper left to lower

Table 1. Operational factors and levels used in testing the FBC design on synthetic wastewater

Factors		Level 1	Level 2	Level 3
A	S/As molar ratio	2.5	2.0	1.5
B	As loading (kg-As m^{-2} h^{-1})	0.2	0.6	1.0
C	PH	2.5	4.0	5.5
D	Feed AS concentration (mg L^{-1})	200	600	1000

* Carrier = 400 g silica sand Superficial velocity = 40 m h^{-1}

Table 2. Fractional design matrix and responses in FBC experiments

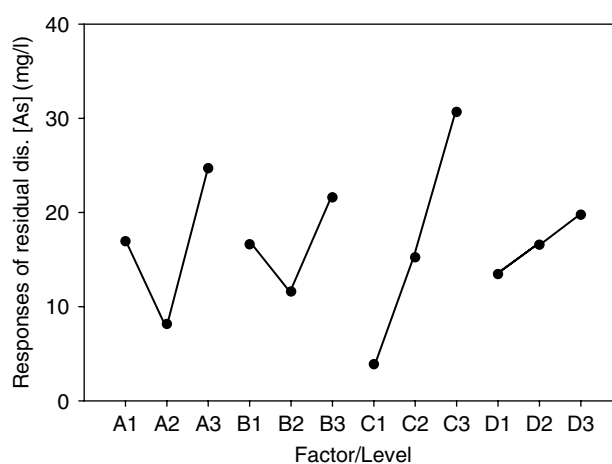|	Factor				Response	
Run	A S/As	B As loading (kg m^{-2} h^{-1})	C pH	D [As]$_{in}$ (mg L^{-1})	Residual dissolved As (mg L^{-1})	Residual total As (mg L^{-1})
1	2.5	0.2	2.5	200	1.1	13.1
2	2.5	0.6	4.0	600	10.6	74.1
3	2.5	1.0	5.5	1000	39.2	167.4
4	2.0	0.2	4.0	1000	10.0	101.6
5	2.0	0.6	5.5	200	14.1	107.5
6	2.0	1.0	2.5	600	0.4	36.0
7	1.5	0.2	5.5	600	38.8	137.0
8	1.5	0.6	2.5	1000	10.1	41.4
9	1.5	1.0	4.0	200	25.2	91.4

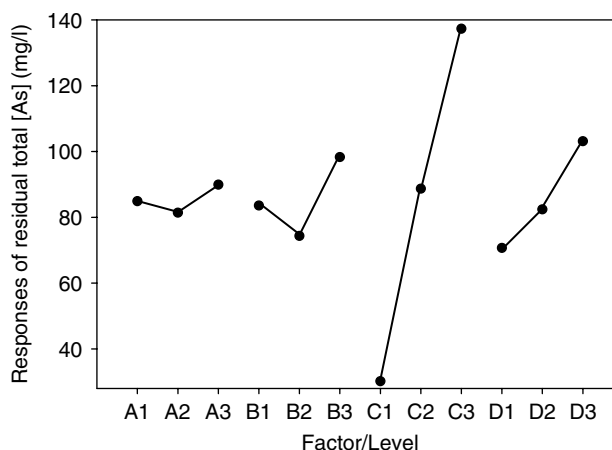**Figure 5.** Residual dissolved As response for each factor/level in L 9 experiment.

Figure 6. Residual total As response for each factor/level in L9 experiment.

right symbolize the crystallization ratio contour plot. The other set is the contour plot of the residual dissolved As concentration. The residual dissolved As concentration achieved at pH 1.6 and S/As ratio 2 met the current HSIP effluent standard (0.5 mg-As
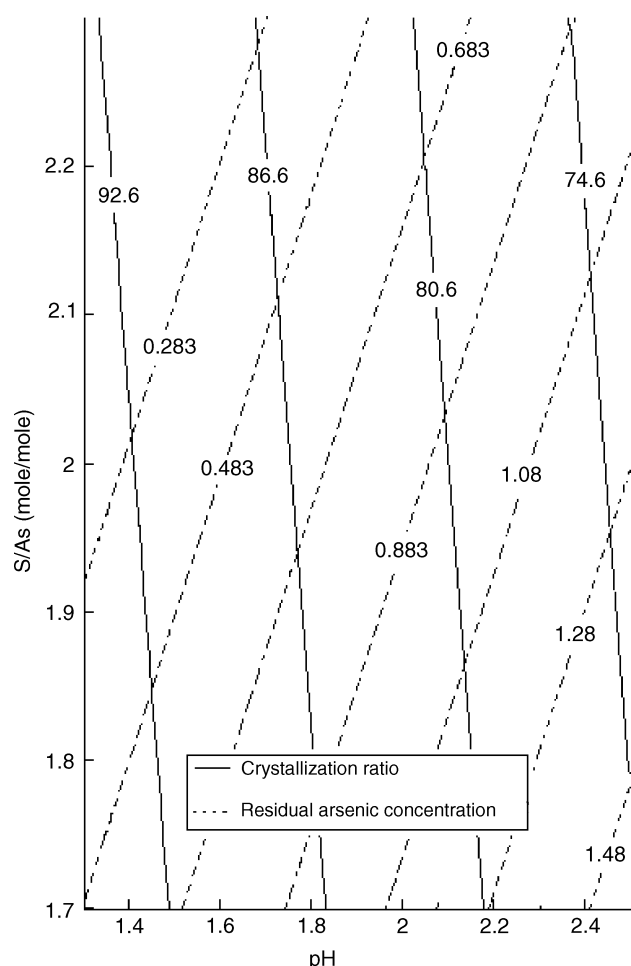
Figure 7. Matlab regression analysis of CSM output of As_2S_3.

Figure 8. Distribution of calculated As in crystallization, precipitation and dissolution at different levels of operational pH.

L^{-1}) and the regulatory discharge limit for industrial wastewater in Taiwan.

The distributions of crystallization/precipitation/dissolution ratio of the effluent As at different operational pH but constant S/As were calculated and are shown in Fig. 8. Greater crystallization and less dissolution were obtained at lower pH values. Thus the dissolution was 7.04% at pH 2.7, in comparison to 0.30% at pH 1.3. The adsorption of arsenic sulfide precipitate on the carrier was the first step to the nucleation of arsenic sulfide crystallization. Better adsorption at lower pH values explained why more crystallization occurred under more acidic conditions. Since the crystallization efficiency of As in the FBC is the key to successful operation, calculation of the crystallization efficiency is demonstrated in the following section.

Crystallization efficiency
The effects of the variables on crystallization efficiency were calculated by referring to the mass balance of As based on the following assumptions:

(1) the system is operated at quasi-steady-state;
(2) crystal growth rates are constant at any time and location;
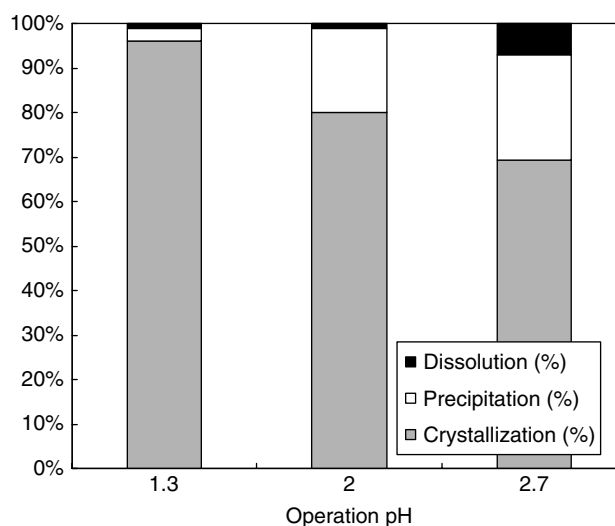(3) suspended As particulates flow out of the reactor steadily;

(4) volume of base and acid added can be neglected compared to the volume of the reactor.

The total As in the reactor is the sum of the quantities of As in the crystals and suspended and soluble arsenic in the effluent:

$$C_w \times Q_w = M_{crystal} + (C_{total} - C_{sol}) \times (Q_w + Q_R)$$
$$+ C_{sol} \times (Q_w + Q_R) \tag{1}$$

where C_w is the As concentration in the feed, $M_{crystal}$ is the growth rate of crystals on the support, C_{total} and C_{sol} are total and soluble As concentrations in the effluent, respectively; Q_w and Q_R represent the respective flow rates of $NaAsO_2$ and Na_2S. Söhnel and Garside[16] suggested that the specific growth rate is proportional to the liner growth rate of the crystal (m s^{-1}). The crystallization efficiency can then be calculated as

$$Crystal (\%) = \{1 - [C_{total} \times (Q_w + Q_R)/C_w \times Q_w]\}$$
$$\times 100\% \tag{2}$$

Prospects for application of FBC in treating As-containing wastewater
This study is a laboratory scale test of the feasibility of using FBC to treat wastewater containing high levels of As. A pilot test based on the results from this study, illustrated in Fig. 9, is currently being underway. A full-scale FBC reactor has been built in Taiwan for wastewater softening. The reactor has a diameter of 2.5 m and is 8 m high with a capacity of $24,000 \, m^3 \, day^{-1}$.

CONCLUSIONS
The potential for treating wastewaters containing high concentrations of As using a fluidized bed crystallization process to $\mu g \, L^{-1}$ levels is investigated.
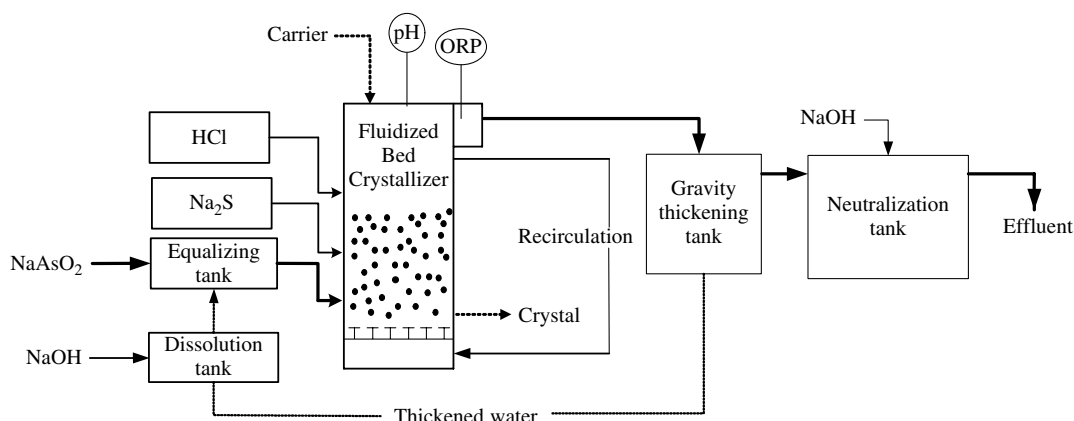
Figure 9. Diagram of FBC process for the treatment of wastewater containing high-strength As.

Sulfide dosage and operational pH are the two most significant parameters in determining the residual As concentration in the effluent. The optimum FBC operating conditions needed to meet the As discharge standard of the HSIP are pH = 2 and S/As = 2.2. Under such conditions the As concentration in the effluent from the FBC reactor can be controlled to <0.5 mg L^{-1}, which meets the regulatory discharge limit for industrial wastewaters in Taiwan. A pilot plant based on the results of this study is currently being tested to treat wastewater with a high concentration of As.

ACKNOWLEDGEMENTS

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