Partial Roasting Technology

June 8th 2017

Challenges and Opportunities in the treatment and management of Arsenic in the Mining Industry in Chile, Santiago de Chile, Chile

presented by Dr. Alexandros Charitos

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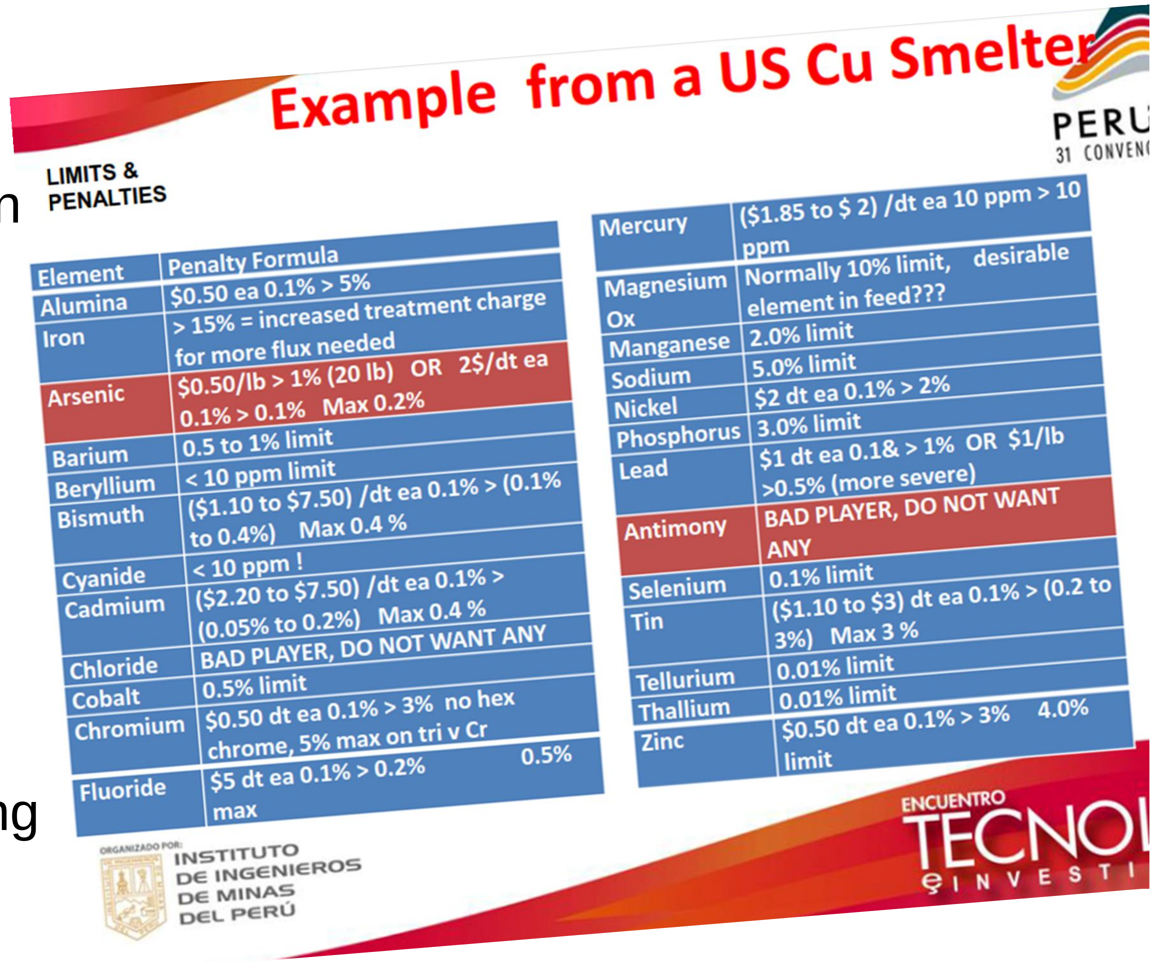
Outotec GmbH & Co. KG, June 2017

Introduction

Why remove impurities prior to Smelting

- Above 10 % of handled concentrates are above penalty levels
- Countries impose limits on As for importing concentrate
- Copper matte will be contaminated with high levels of As
- Arsenic will be distributed to all outgoing material streams potentially causing health issues and environmental problems



Example from a US Cu Smelter

LIMITS & PENALTIES

Element	Penalty Formula
Alumina	$0.50 ea 0.1% > 5%
Iron	> 15% = increased treatment charge for more flux needed
Arsenic	$0.50/lb > 1% (20 lb) OR 2$/dt ea 0.1% > 0.1% Max 0.2%
Barium	0.5 to 1% limit
Beryllium	< 10 ppm limit
Bismuth	($1.10 to $7.50) /dt ea 0.1% > (0.1% to 0.4%) Max 0.4 %
Cyanide	< 10 ppm !
Cadmium	($2.20 to $7.50) /dt ea 0.1% > (0.05% to 0.2%) Max 0.4 %
Chloride	BAD PLAYER, DO NOT WANT ANY
Cobalt	0.5% limit
Chromium	$0.50 dt ea 0.1% > 3% no hex chrome, 5% max on tri v Cr
Fluoride	$5 dt ea 0.1% > 0.2% 0.5% max

Mercury	($1.85 to $ 2) /dt ea 10 ppm > 10 ppm
Magnesium Ox	Normally 10% limit, desirable element in feed???
Manganese	2.0% limit
Sodium	5.0% limit
Nickel	$2 dt ea 0.1% > 2%
Phosphorus	3.0% limit
Lead	$1 dt ea 0.1& > 1% OR $1/lb >0.5% (more severe)
Antimony	BAD PLAYER, DO NOT WANT ANY
Selenium	0.1% limit
Tin	($1.10 to $3) dt ea 0.1% > (0.2 to 3%) Max 3 %
Tellurium	0.01% limit
Thallium	0.01% limit
Zinc	$0.50 dt ea 0.1% > 3% 4.0% limit

Partial Roasting Solution before smelting

- Arsenic content in feed can be reduced from
  - $\Rightarrow$ more than 12 wt.-% down to < 0.3 wt% in the roasted calcine
  - $\Rightarrow$ The calcine can be directed to a smelter or sold to the market

- Sulphuric acid as saleable byproduct with low Arsenic content < 1 ppm

De-arsenifying Roasting for Copper concentrates

Client	Start	Capacity tpd	sulphur content Feed → Calcine wt%		Arsenic content Feed → Calcine wt%	
Boliden	1980	1080	25-30	16-20	2.5	0.2
Lepanto	1983	180	34	22	10-12	0.3
Codelco	2013	1700	34	22	5.8	< 0.3

✓Outotec has built more than 300 fluidized bed roasters

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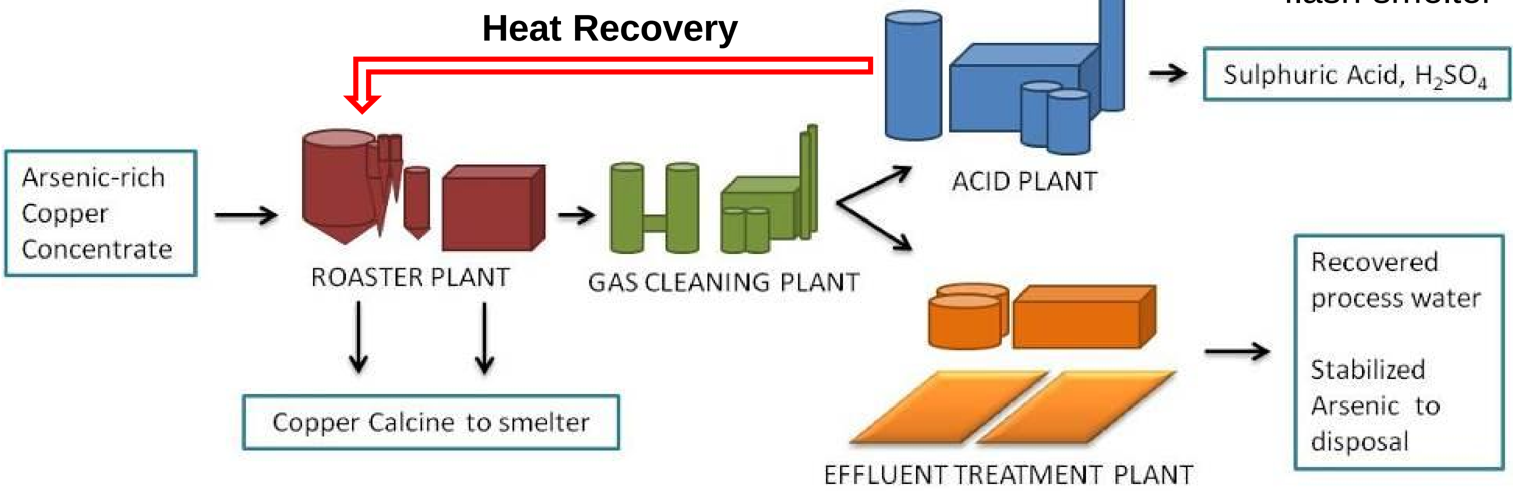
General Partial Roasting Flowsheet

- Pyrometallurgical route for calcine de-arsenification:
  ⇒ Route followed in Codelco DMH roaster

Roaster Plant
- As volatilization
- **As concentrate 3-5.8 wt.-%**
- **As in calcine: < 0.3 wt.-%**

Gas Cleaning
- Final dedusting
- **As recovery in effluent**

sulphuric Acid Plant
- Possibility of heat recovery
  ⇒ More S in calcine
  ⇒ Better heat recovery in flash smelter



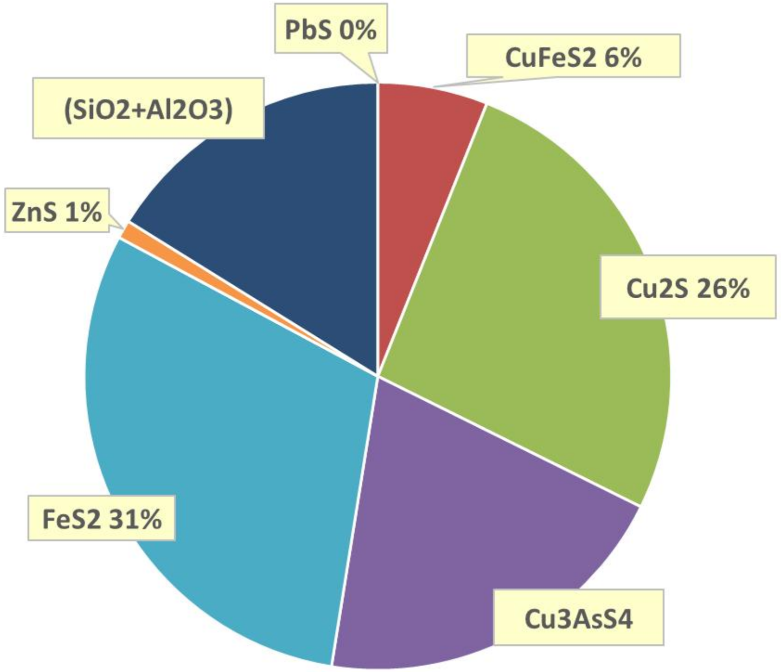
Effluent Treatment Plant
- **Arsenic stabililization as ferric arsenate or calcium arsenite**

Arsenic containing concentrates

- Enargite rich deposits are common in Chile and South America

  ⇒ *The Codelco DMH concentrate which is rich in Enargite (Cu_3AsS_4) is not unique!*

DMH Concentrate Mineralogy



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Example

Codelco DMH Roaster

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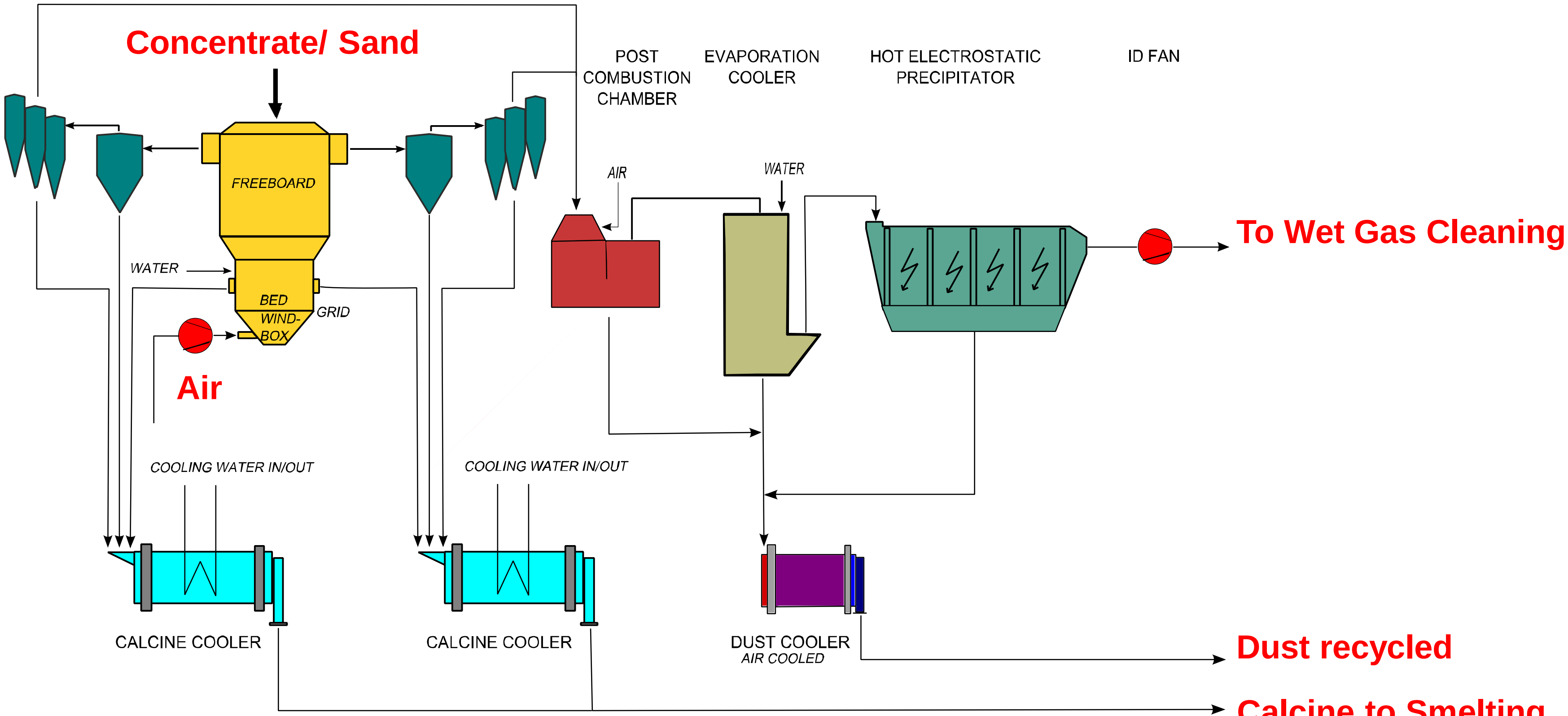
Codelco DMH Roaster - Flowsheet

Gas Phase:

ROASTER → CYCLONES → PC CHAMBER → EV.COOLER → H-ESP → GAS CLEANING

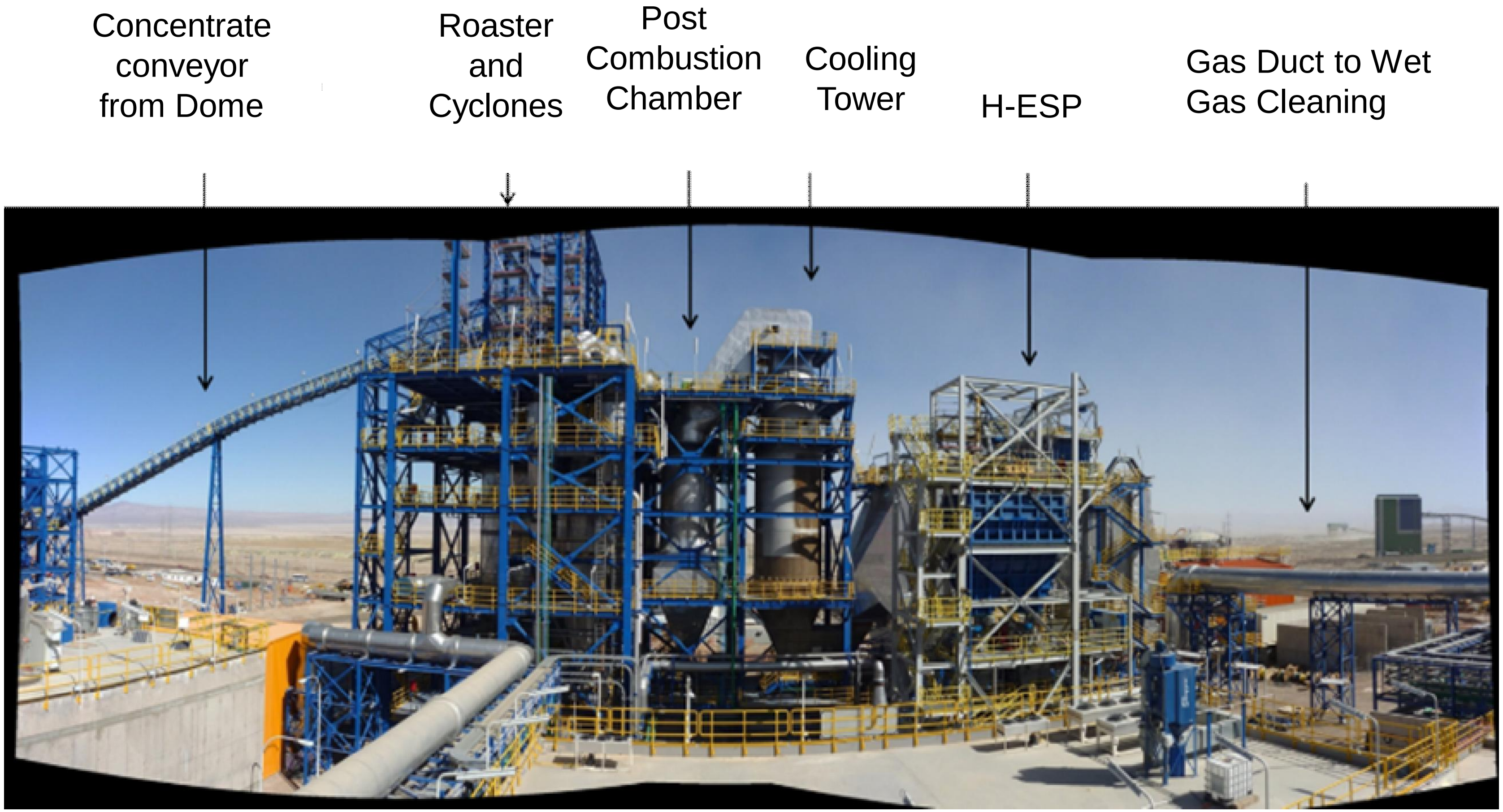


Solid Phase

ROASTER → OVERFLOW/ CYCLONES → CALCINE COOLERS→ TO SMELTING

Codelco DMH Roaster Plant

Plant capacity 550 ktpy concentrate (Cu 29 wt%; As 5.8 wt%)



Codelco DMH Roaster Peformance - Elimination of bed sintering

- **Bed sintering had been a challenge during commissioning (2014)**
  - Has been a result of melted phases in tuyere air vicinity
  - Encountered after shutdowns
- **Analysis of sintered probes revealed**:
  - Hot spots of 1200 – 1400°C locally (from mineralogical analysis)

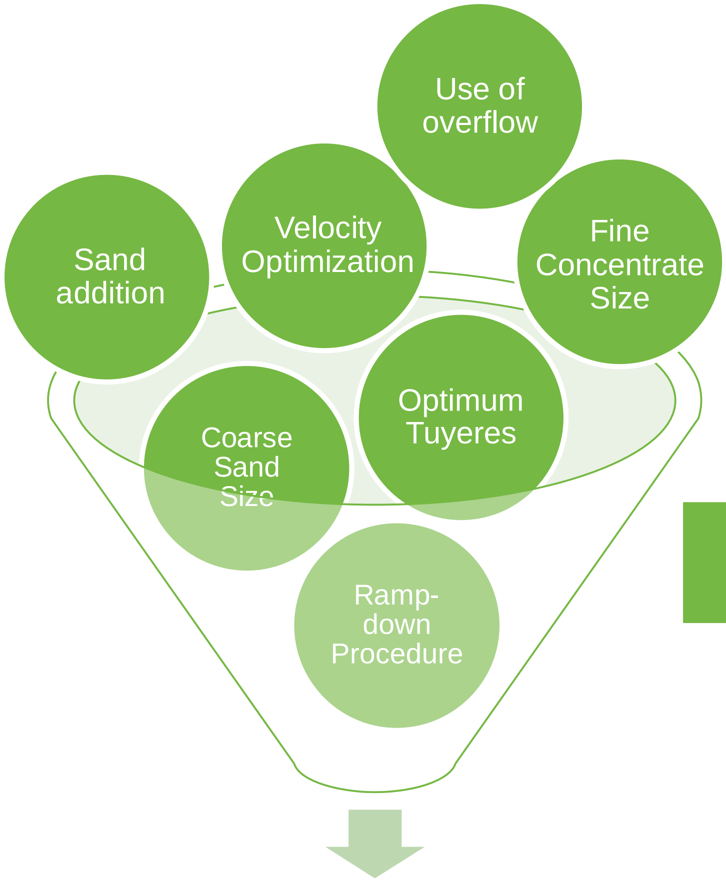
    ⇒ from high sulphur and oxygen in the tuyere vicinity
  - A sand (SiO_2) content of only 30 wt.-%
- **Eliminating sintering required**
  - Not allowing hotspots to occur
  - Increase the sand (SiO_2) content

    ⇒ to obtain an inert bed

Layer of sintered nozzles

No longer possible through fluidization engineering measures

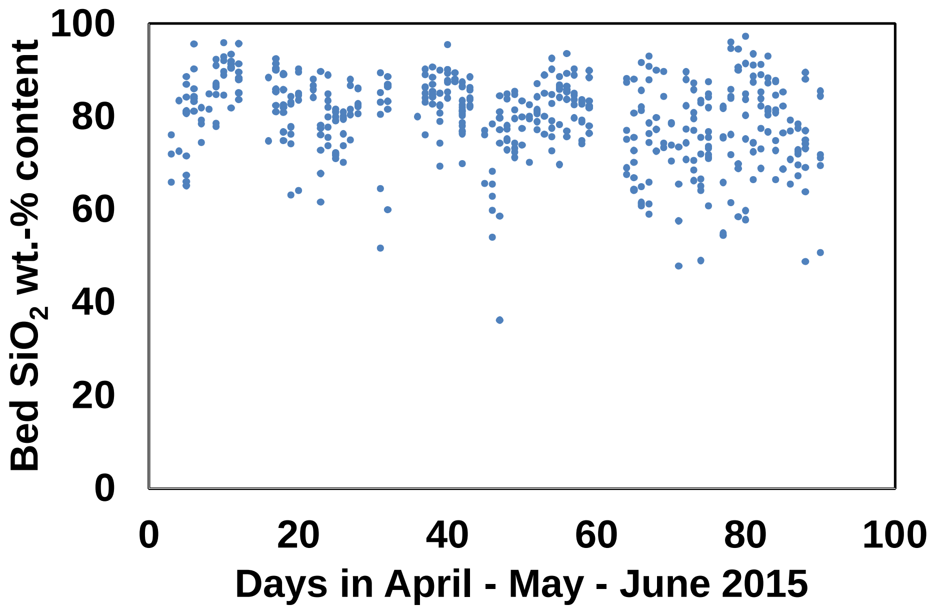
Fluidized Bed Key Operating Factors



Sand rich - inactive bed > 70 wt.-%
= no sintering chance

- Elimination of bed sintering through engineering measures

  ⇒ Introducing inert material as bottom bed layer



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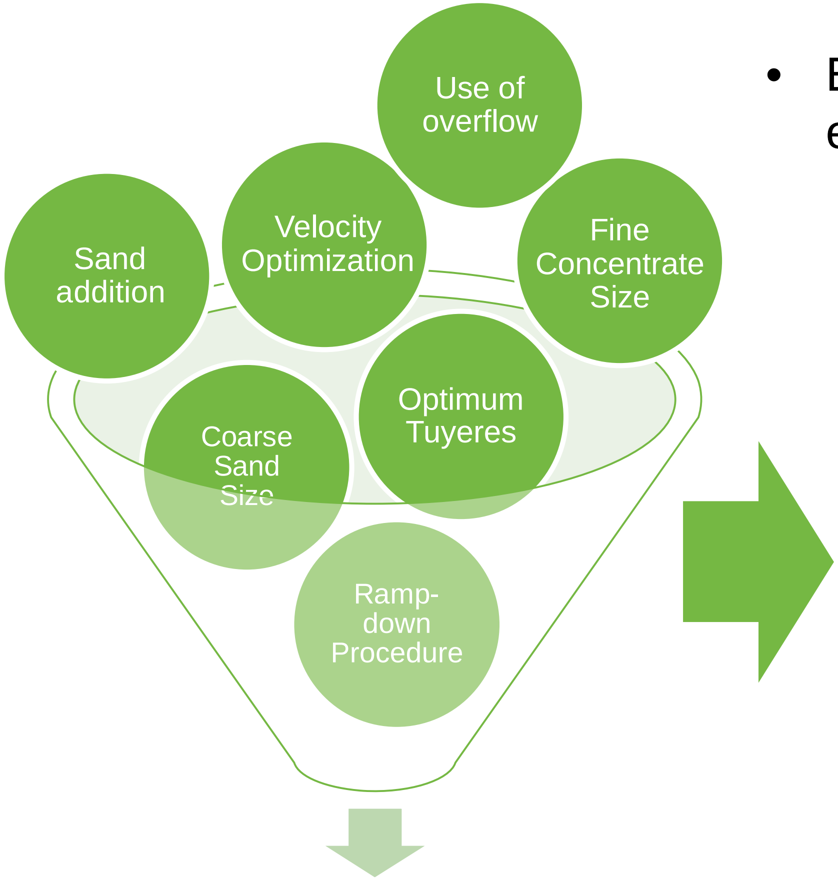

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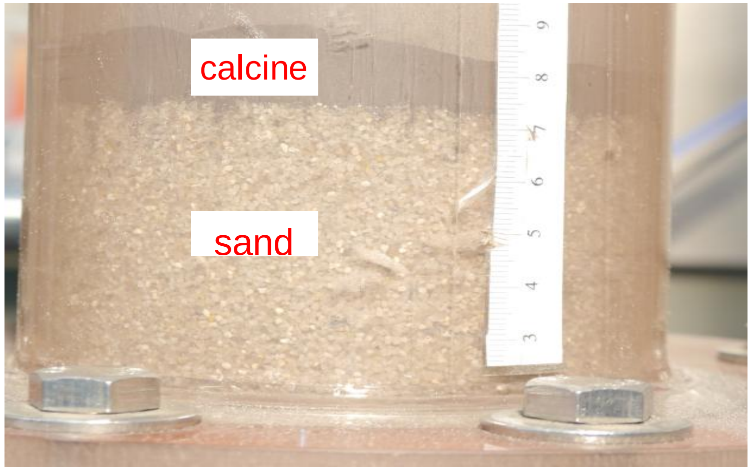
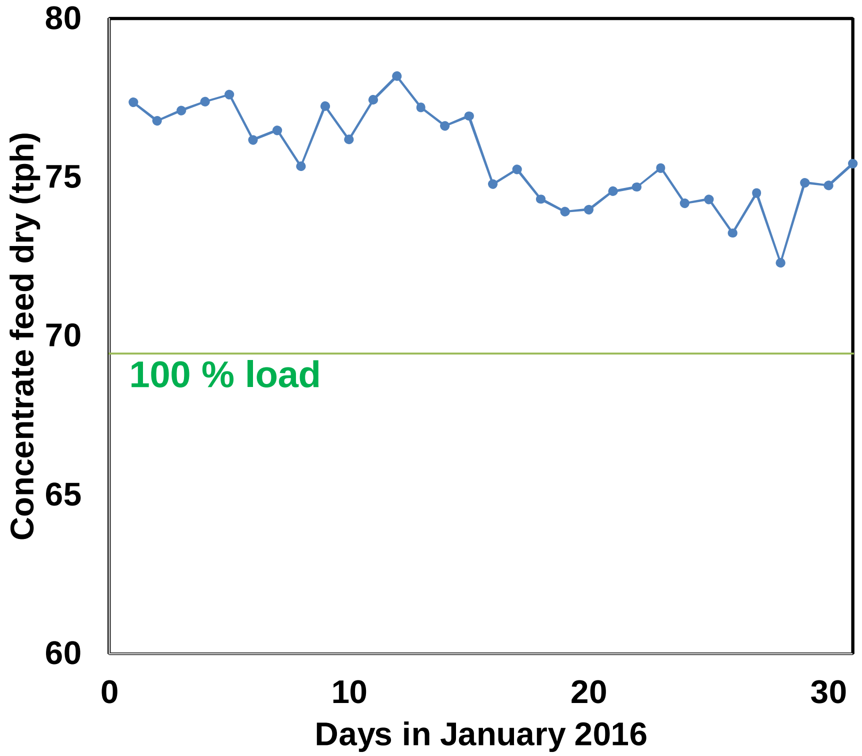
Bed after blower ramp-down



Codelco DMH Roaster – Capacity



- Codelco DMH capacity is:
  - Around 75 tph dry feed
- Codelco DMH capacity is:
  - At the 110 % load line
  - Always above 100 % load
- Further solids to the roaster
  - Additional silica sand (< 10 wt.-% of feed)
  - **Sand required to form a bottom inert bed within the roaster**
    - ⇒ Thereby, hotspots and bed sintering is avoided

✓ **The Codelco DMH roaster operates above 100 % load**

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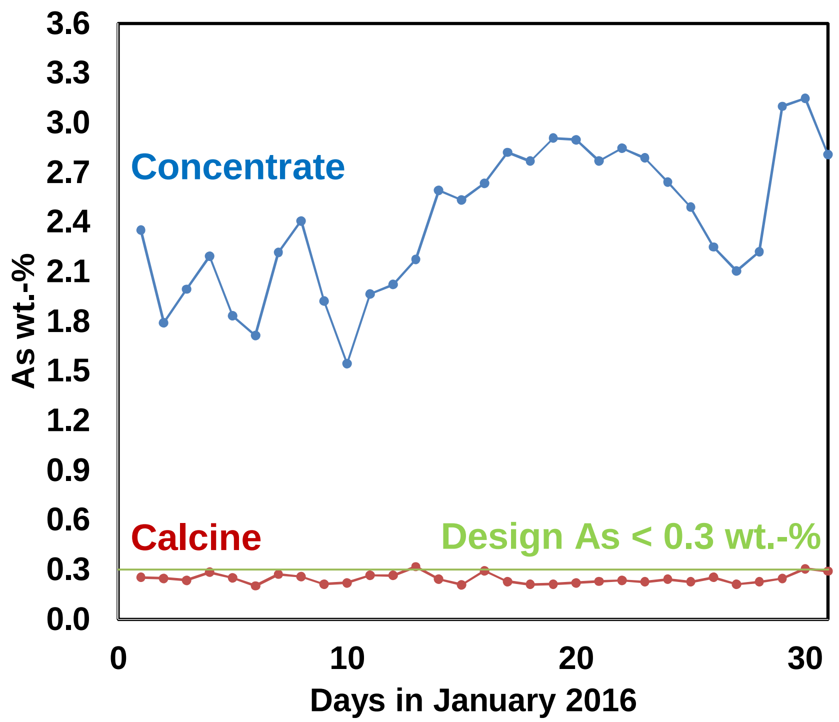
Codelco DMH Roaster – As removal



- Concentrate inlet As levels are
  - At the 3 wt.-% level
- Codelco DMH As calcine level is
  - 0.2 – 0.3 wt.-%
    - ⇒ at above 100 % load
    - ⇒ Despite feed As concentration fluctuation
- Main de-arsenifying reaction:

$$2Cu_3AsS_4(s) \rightarrow As_2S_3(g) + 3Cu_2S(s) + S_2(g)$$

✓ **The Codelco DMH roaster exceeds the product quality design**

✓ **In addition antimony (Sb) removal is approx. 60 – 70 %**

Gas Cleaning of partial roaster off-gases

Technical Grade Sulphuric Acid

- Nasty impurities increase:

  ⇒ *Arsenic, Hydrogen Chloride, Hydrogen Fluoride, Mercury, Selenium*

  ✓ *However, acid quality has to be sustained!*

Impurity	
Appearance	Water Clear
Colour	40 Hazen
Hg (Mercury)	< 0.5 ppm
Fe (Iron)	< 25 ppm
Ni (Nickel)	< 1 ppm
Cr (Chromium)	< 1.5 ppm
Mn (Manganese)	< 0.3 ppm
SO_2 (Sulph. Diox.)	< 30 ppm
Cl^- (Chloride)	< 2 ppm
F^- (Fluoride)	< 5 ppm

Impurity	
NH_4^+ (Ammonium)	< 1 ppm
NO_3^- (Nitrate)	< 5 ppm
As (Arsenic)	< 1 ppm
Cu (Copper)	< 0.2 ppm
Cd (Cadmium)	< 0.02 ppm
Pb (Lead)	< 0.3 ppm
Zn (Zinc)	< 0.1 ppm
Sb (Antimony)	< 0.02 ppm
Bi (Bismuth)	< 0.02 ppm
Se (Selenium)	< 0.1 ppm

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Typical Flowsheet for Partial Roasting

OTOVENT Quench

- Cools gases to saturation
- Allows for As particles to agglomerate

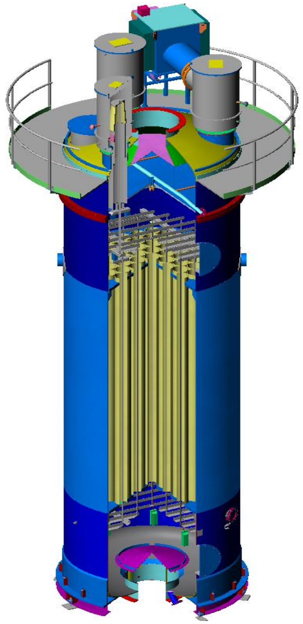
High Efficiency Scrubber

- **Allows for adjustable pressure drop**
- As particles to effluent

Cooling Tower

- Water removal by cooling
- Conditioning of Acid concentration

Wet ESPs

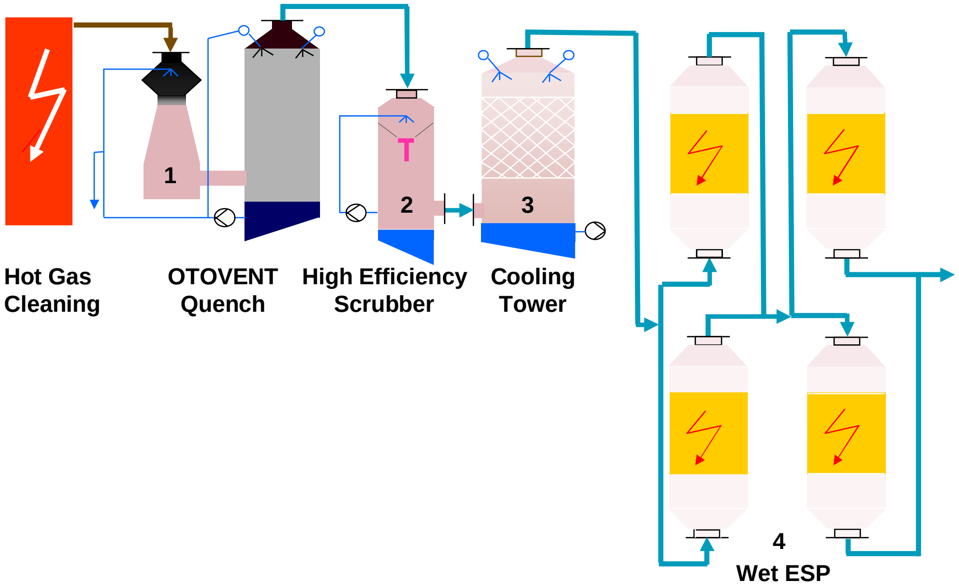


- Removal efficiency

Dust > 99.9 %

Acid Mist > 99.7 %

Impurity Removal from gases

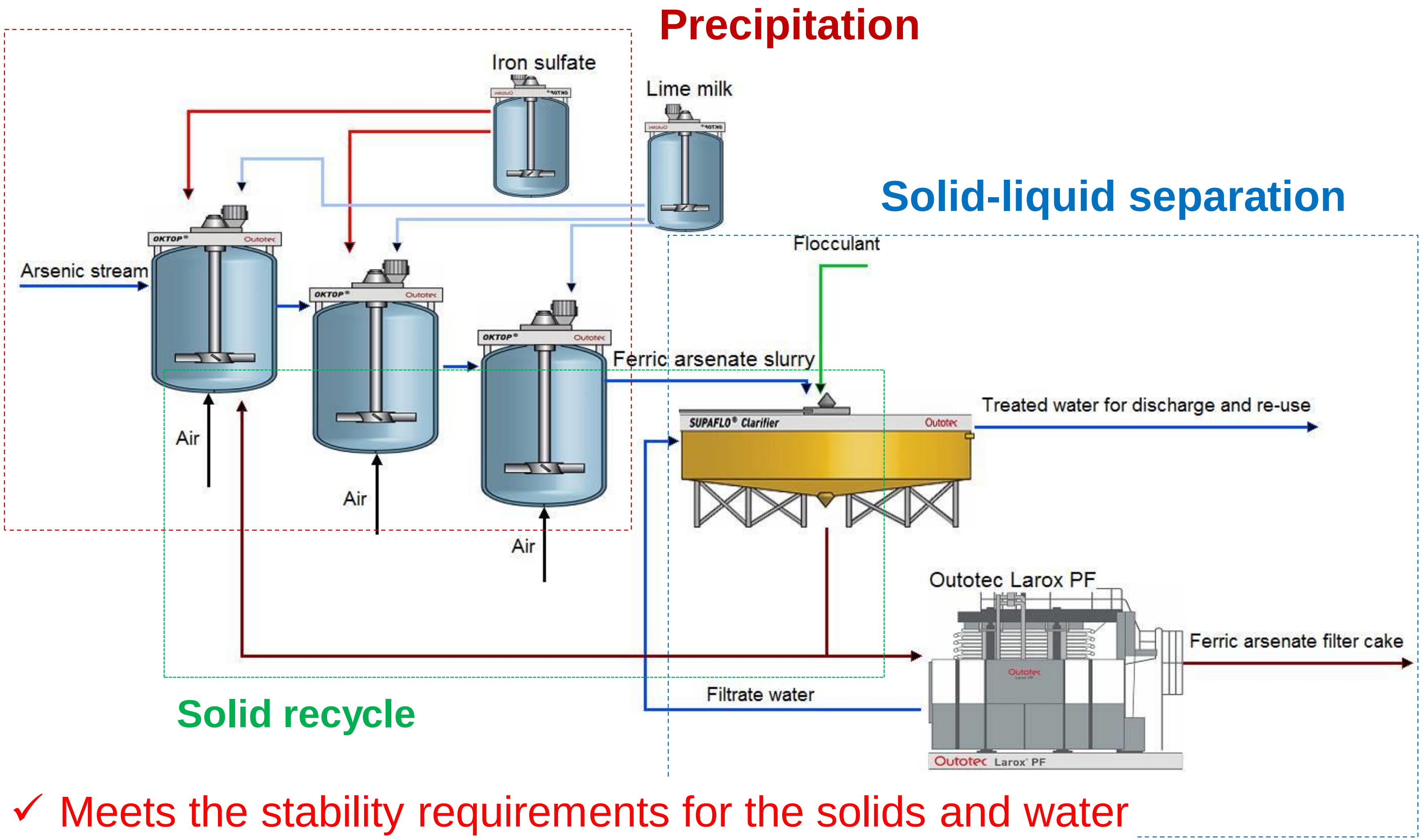


- ✓ As in effluent bleed as $HAsO_2$
- ✓ As in acid < 1 ppm
- ✓ No emissions at stack

	Dust	Fumes	Acid	Wat er	Halides	Mercury	Own Technology
	Si, Cu, Zn, Fe, Pb	As, Cd, Se, Sb, Bi	H_2SO_4 Mist	H_2O	Cl, F	Hg	
1 Quench Tower	< 50 %	< 30 %	< 30 %	0	0	0	OTO
2. Scrubber	< 95 %	< 90 %	< 50 %	0	0	0	OTO
3. Gas Cooling Tower	0	0	0	Yes	Yes	0	OTO
5. Wet ESP	> 90 %	> 99 %	> 99 %	Yes	0	Yes	OTO

Effluent treatment plant

Ferric Arsenate Precipitation Process



✓ Meets the stability requirements for the solids and water

⇒ Passes TCLP and CEN tests

Ferric Arsenate Precipitation Process

- Iron oxidation Ferrous to Ferric iron :

$$4\ Fe^{2+} + O_2\ (g) + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$$

- Arsenic oxidation (As^{3+} to As^{5+}) :

$$HAsO_2(aq) + \frac{1}{2}\ O_2\ (g) + H_2O \rightarrow H_3AsO_4(aq)$$

Oxidation steps

- Ferric Arsenate precipitation reaction :

$$4HAsO_2 + 4FeSO_4 + 2H_2O + 3O_2(g) \rightarrow 4FeAsO_4 + 4H_2SO_4$$

Optimum pH for this process is 4 - 4.5

Arsenic precipitation

- Acid is neutralized according to:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4.2H_2O$$

- Metal impurities present will precipitate according to:

$$Ca(OH)_2 + Me^{2+}/Me^{3+} \rightarrow Me(OH)_2\ /\ Me(OH)_3 + CaSO_4$$

Optimum pH for this process is above 8.0

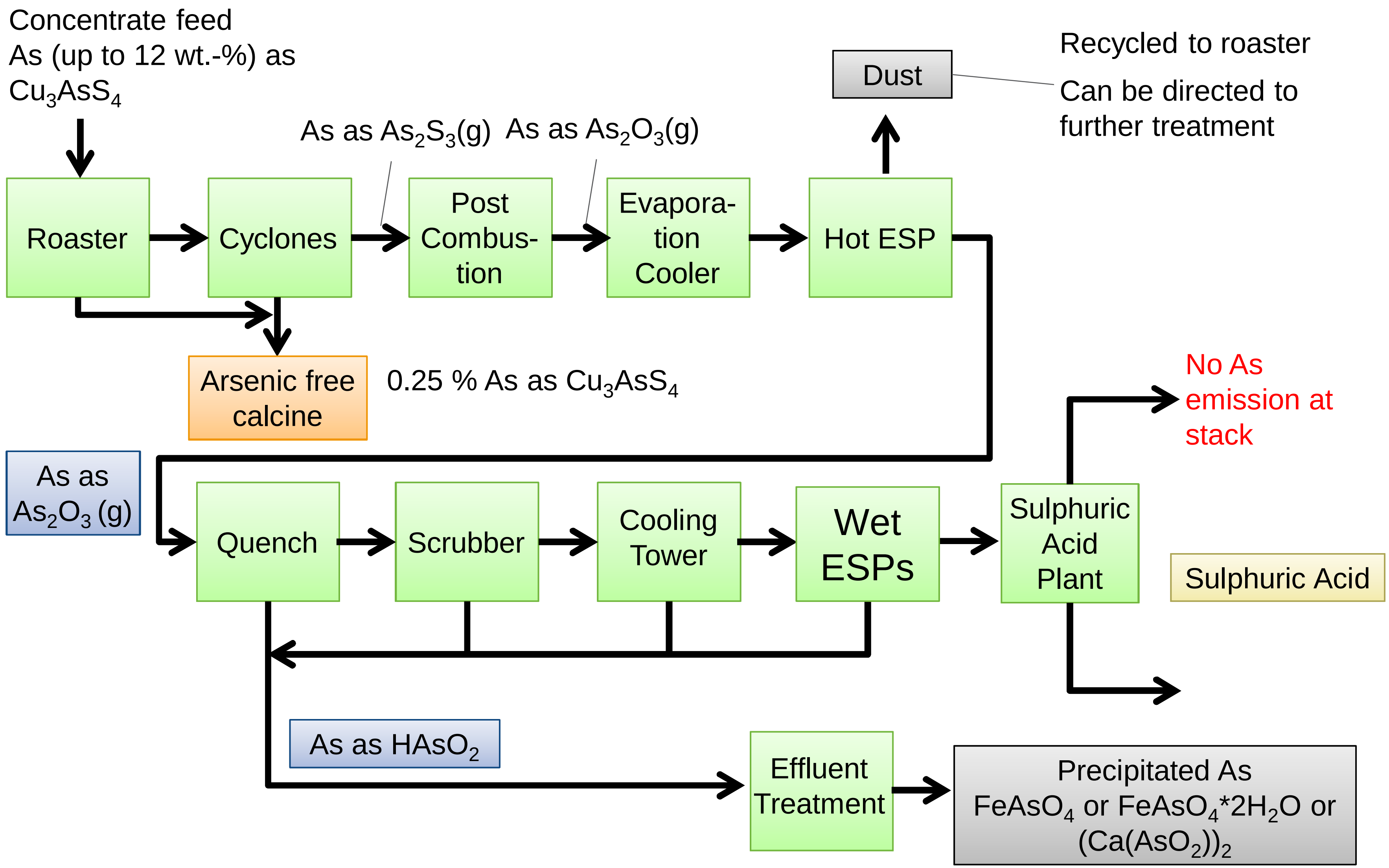
Additional reactions

Ferric arsenate Precipitation Process

Outotec's Ferric Arsenate process / installed in Finland

Summary

Summary – Fate of As



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Outlook

Outlook

- **Partial Roasting at the forefront**
  - ⇒ allows for As- rich concentrates treatment to clean concentrate
  - ⇒Allows for production of marketable acid
- **Pyrometallurgical flue dust treatment**
  - ⇒ through combination with partial roaster
  - ⇒ OR through dedicated small roaster unit at a smelter with no partial roaster

✓ *Roasting – Gas Cleaning – Acid Plant & As stabilization in the effluent treatment plant is a sustainable route to process arsenic*

✓*The successful operation of the DMH roaster is a monument of Chilean – European mutual cooperation*

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Sustainable use of
Earth's natural resources