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Thermodynamics of Selective Roasting of Arsenic from Tennantite Containing Copper Concentrates



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Minor elements are a key issue for sustainable metal production



Context

- Australia exports ~ 3 millions of tpa of base metals in form of concentrate and refined metals.
- Base metal ores contain low levels (1- 10⁴ ppm) of toxic/hazardous elements (As, Sb, Bi, Cd, Hg, Se, Te, Po, Th, U, ..)
- Smelters impose treatment charges and penalty payment on minor elements in concentrates and reject those beyond the level they can safely process
- Ore bodies of future are more complex, finer-grained and contain higher amount of minor/toxic elements.

Accumulated mass of minor elements in biosphere is large and could have a significant environmental impact

Management of Minor/Toxic Elements



Imperative to develop alternative treatments for selective removal of toxic elements at the mine site before despatch of concentrate to smelters

Strategies and practices are needed for dealing with processing of future ores

- Early removal and safe disposal
- Improved practices to control department of minors in current processes

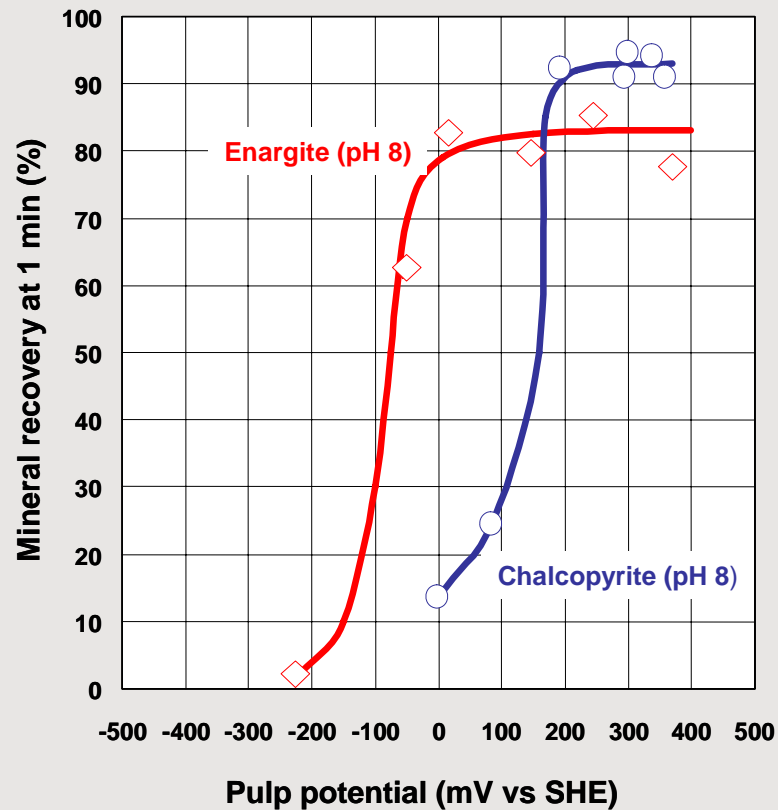
An Arsenic flowsheet



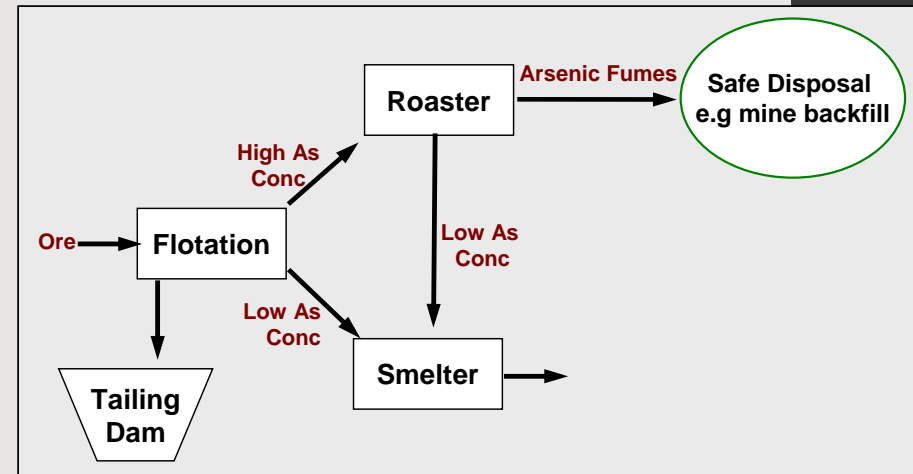
- Arsenic (As) removal from ores/concentrates through selective floatation of As minerals developed at CSIRO in 90's
 - Publication embargoed until recently.
- Conceptual flowsheet for early removal and safe disposal of arsenic was published in 2006 and became focus of a CSRP Foundation project
 - Floatation evaluated on a NSW High As, copper ore
 - As was in the mineral tennantite ($\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}$)
 - Low As and high As concentrates were produced
 - Investigate selective roasting to remove As from the high As concentrate
 - Thermodynamic approach to evaluate optimum conditions
 - Experimental component to evaluate kinetics or unforeseen problems.

Early Removal and Safe Disposal

Selective mineral recovery in 1 minute



Conceptual flowsheet



Recent tests have achieved >70% selectivity with some Australian ores

As removal from high As Concentrate



- As locked up in a high copper mineral
 - Tennantite ($\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13}$)
 - Part of a family of related minerals
 - $(\text{Cu,Ag})_{10}(\text{Cu,Fe,Zn})_2(\text{As,Sb})_4\text{S}_{13}$
 - Decomposes under an inert atmosphere when heated:
 - $\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13} = 5\text{Cu}_2\text{S} + 2\text{FeS} + \text{As}_4\text{S}_4(\text{g}) + \text{S}_2(\text{g})$
 - $\text{As}_4\text{S}_4(\text{g})$ pressure varies with temperature (1 atm at $\sim 660^\circ\text{C}$)
- Potential of the flow sheet
 - Capture arsenic fume in a concentrated stream
 - Remove As without destroying fuel value of concentrate
 - Reduce smelter penalties for concentrate producers

Thermodynamic modelling



- Gibbs Free Energy minimisation to determine stable species & phases
 - Emphasis on As species, and reactions of the major compounds in the concentrate.
 - Included volatile sulphide, elemental and oxide species
 - Solid phases assumed to be pure and at unit activity
 - No solid solutions modelled
 - Investigating conditions to find optimum As volatilisation
 - Temperature
 - Sulphur dioxide (SO₂) concentration
 - Partial combustion of concentrate
 - Sulphidising agent (FeS₂)
 - Emphasis on neutral or partial roasting

Defined species/phases



Gas	species			Solids	
N ₂	As ₅	FeS	Cu ₁₀ Fe ₂ As ₄ S ₁₃	Cu ₂ S	CaS
O ₂	As ₄ S ₄	Cu O	Cu ₅ FeS ₄	Cu ₂ O	CaSO ₄
SO ₂	As	Cl	CuFe S ₂	Cu ₂ SO ₅	CaSO ₃
SO ₃	As ₂	Cl ₂	FeS ₂	Fe	CaCl ₂
S	As ₃	HCl	CaO	FeO	
S ₂	As ₄	Ca	MgO	Fe ₂ O ₃	Liquids
S ₃	As ₄ O ₆		SiO ₂	Fe ₃ O ₄	H ₂ O
S ₄	AsH ₃		Al ₂ O ₃	Fe ₂ S ₃ O ₁₂	
S ₅	As Cl ₃		Cu	FeSO ₄	
S ₆	H ₂		CuO	FeS	
S ₇	H ₂ O		CuS	Ca ₃ As ₂ O ₈	
S ₈	H ₂ S		CuSO ₄	Fe ₃ As ₇ O ₈	

As volatilises as ?



■ Over the range of temperature, and gas composition

■ Major As gaseous species were:

- As_4S_4 , As_4
- Proportions change with temperature and pS_2

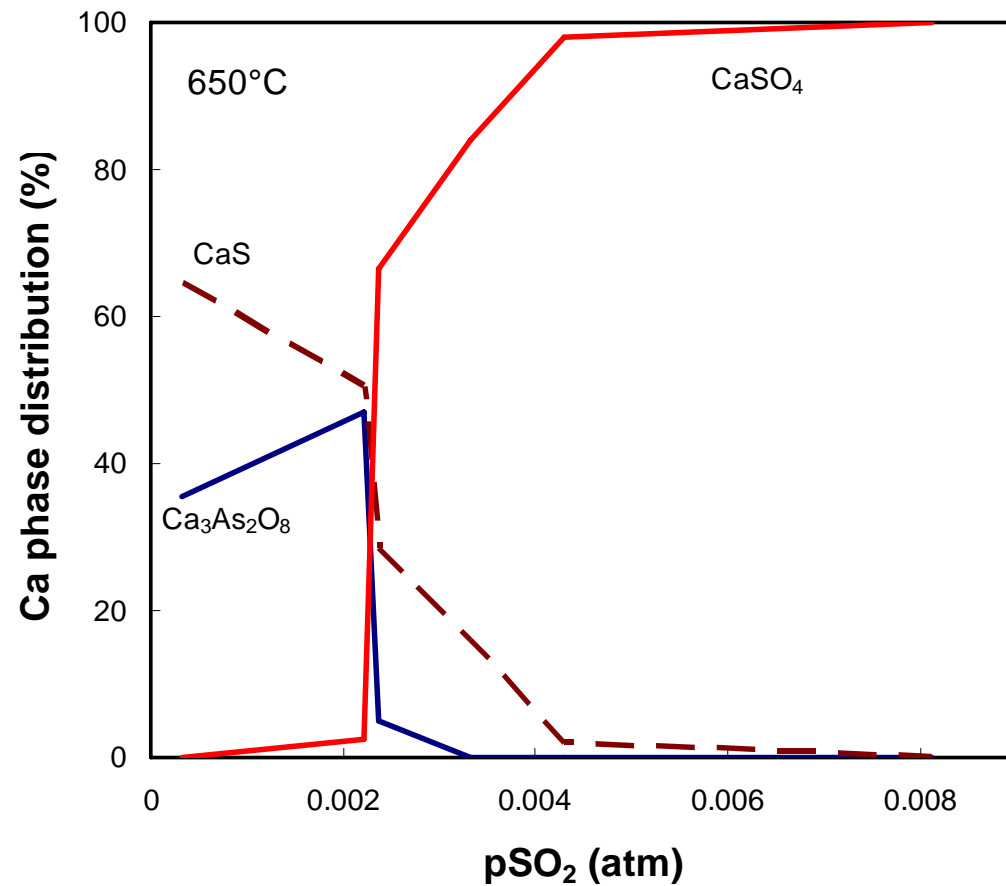
■ Trace levels of:

- AsS , As_2 and As_3

Temp (°C)	600	700	800
pS_2 (atm)	1.4×10^{-4}	3×10^{-4}	7×10^{-4}
Gaseous As distribution (mol%)			
As_4S_4	52.3	60.6	80.0
As_4	47.7	39.0	19.0
AsS	0.01	0.06	0.20
As_2	0.04	0.27	0.86
As_3		0.01	0.03

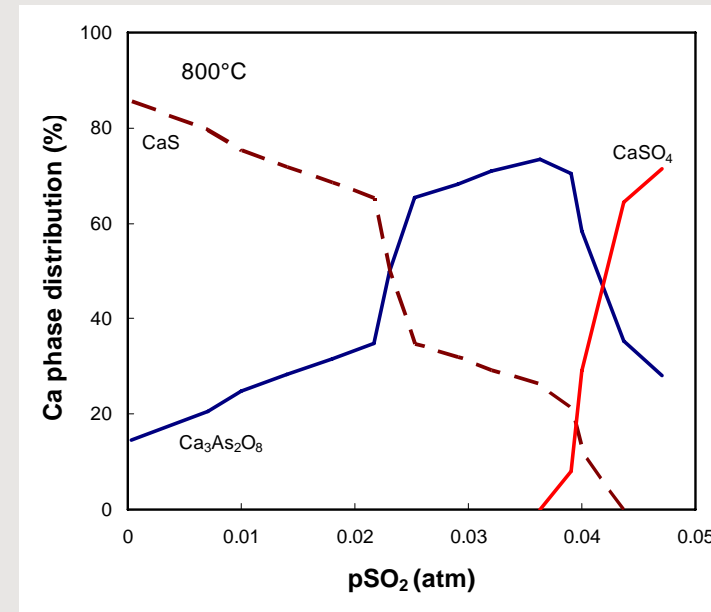
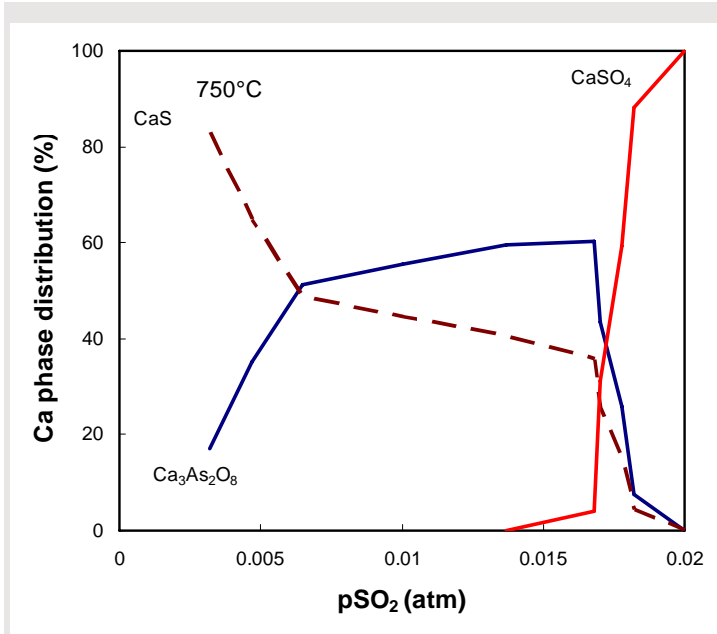
■ Calculations confirm As_4S_4 (g) major species of Tenantite decomposition

When tennantite decomposes



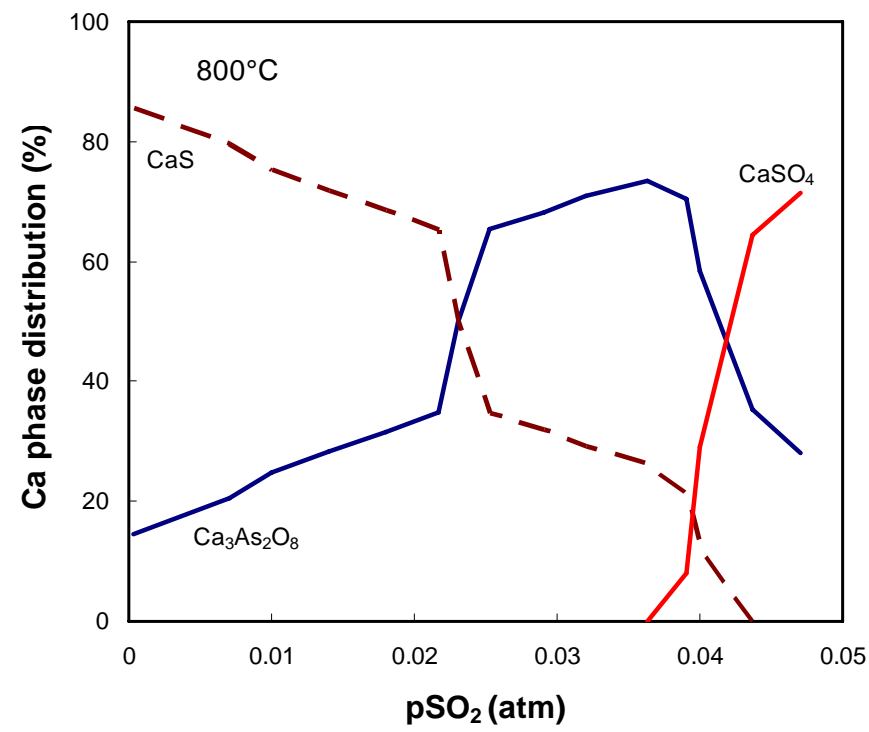
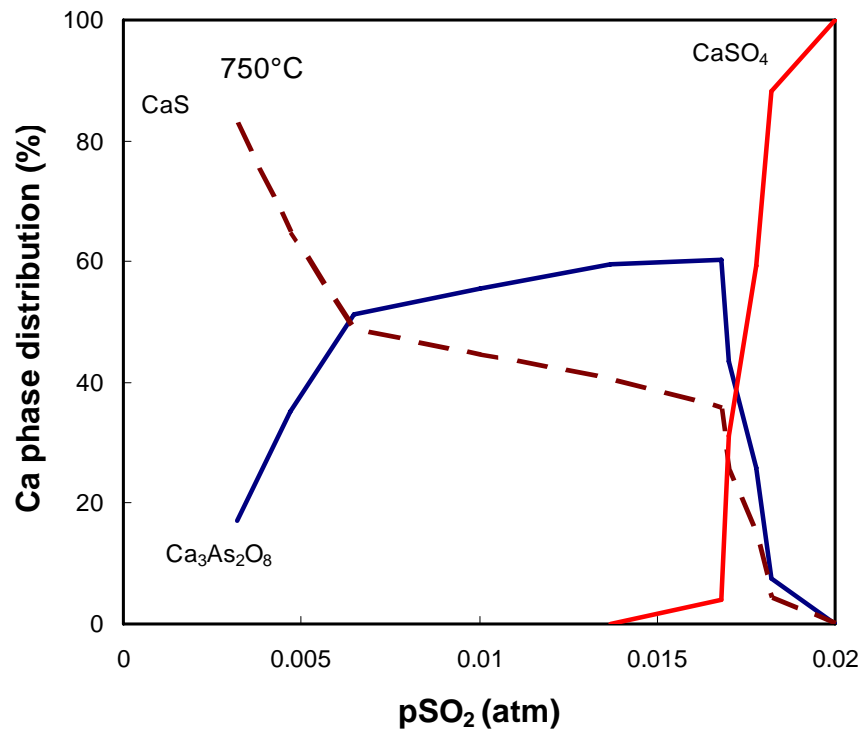
- As forms a stable calcium compound
- As deportment depends on $\text{Ca}_3\text{As}_2\text{O}_8$ stability

Calcium arsenate stability is the key



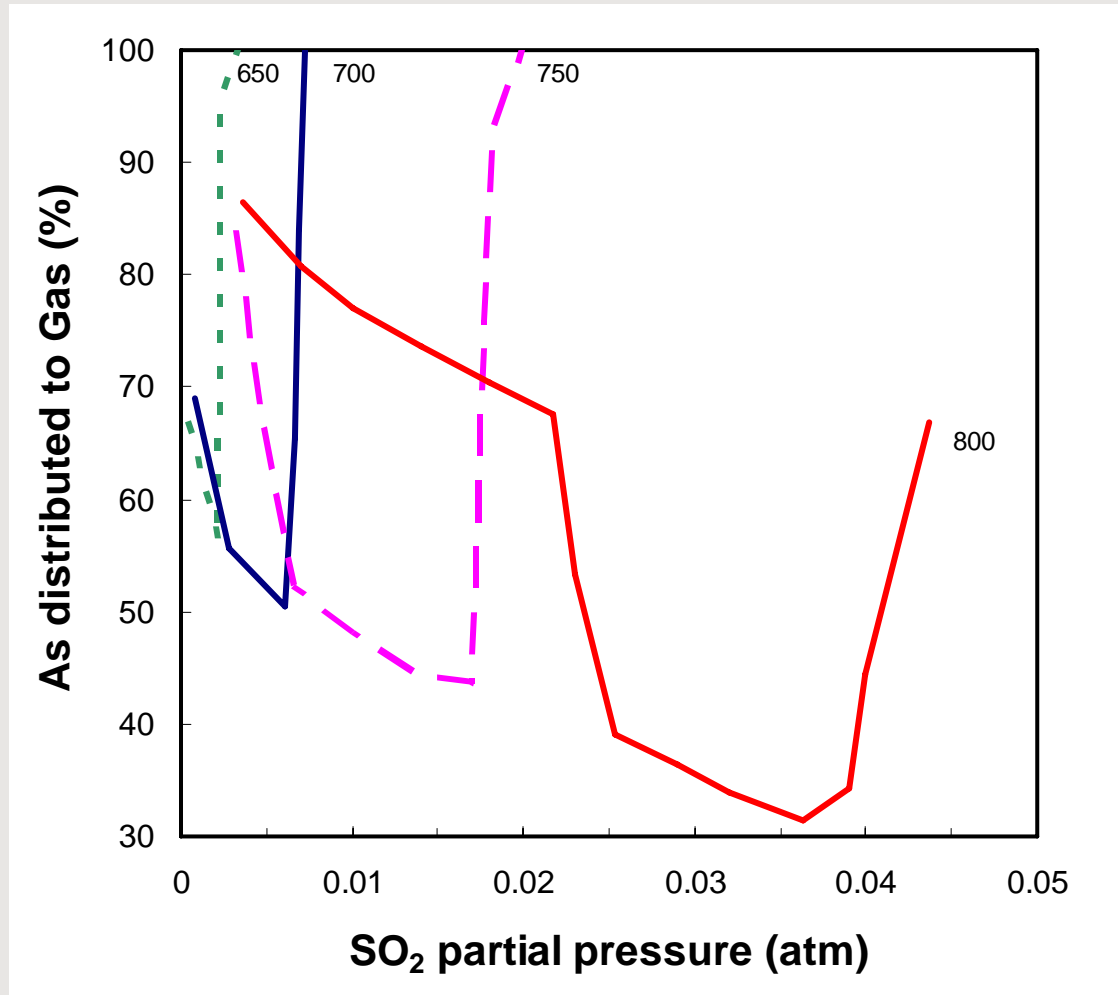
- Thermodynamics controlled by $\text{CaS}/\text{Ca}_3\text{As}_2\text{O}_8/\text{CaSO}_4$
 - $6\text{CaS} + \text{As}_4\text{S}_4 + 8\text{O}_2 = 2\text{Ca}_3\text{As}_2\text{O}_8 + 5\text{S}_2$ $\Delta G = -2257.5 \text{ kJ at } 700^\circ\text{C}$
 - $6\text{CaS} + \text{As}_4 + 4\text{O}_2 = 2\text{Ca}_3\text{As}_2\text{O}_8 + 3\text{S}_2$ $\Delta G = -2392.4 \text{ kJ at } 700^\circ\text{C}$
 - $2\text{Ca}_3\text{As}_2\text{O}_8 + 5\text{S}_2 + 4\text{O}_2 = 6\text{CaSO}_4 + \text{As}_4\text{S}_4$ $\Delta G = -1422.8 \text{ kJ at } 700^\circ\text{C}$
 - $2\text{Ca}_3\text{As}_2\text{O}_8 + 3\text{S}_2 + 4\text{O}_2 = 6\text{CaSO}_4 + \text{As}_4$ $\Delta G = -1287.9 \text{ kJ at } 700^\circ\text{C}$

Calcium arsenate stability is the key



- Thermodynamics controlled by $\text{CaS}/\text{Ca}_3\text{As}_2\text{O}_8/\text{CaSO}_4$

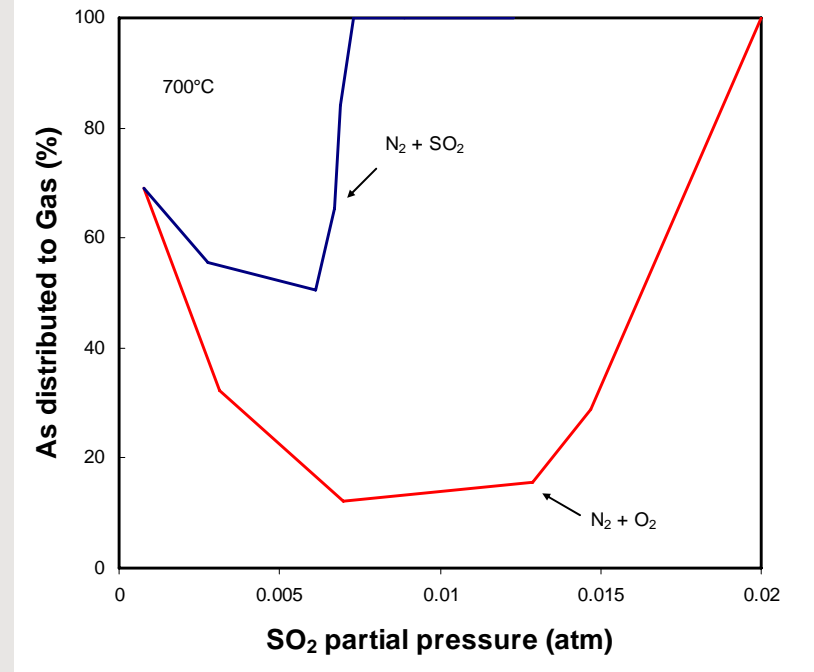
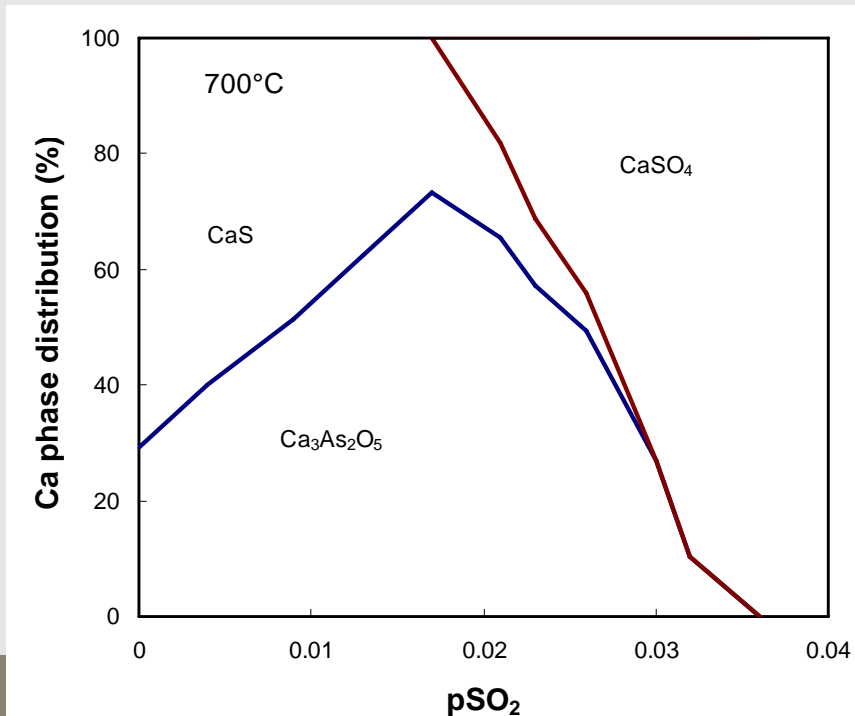
and affects As gaseous deproportion



Partial roasting of the concentrate

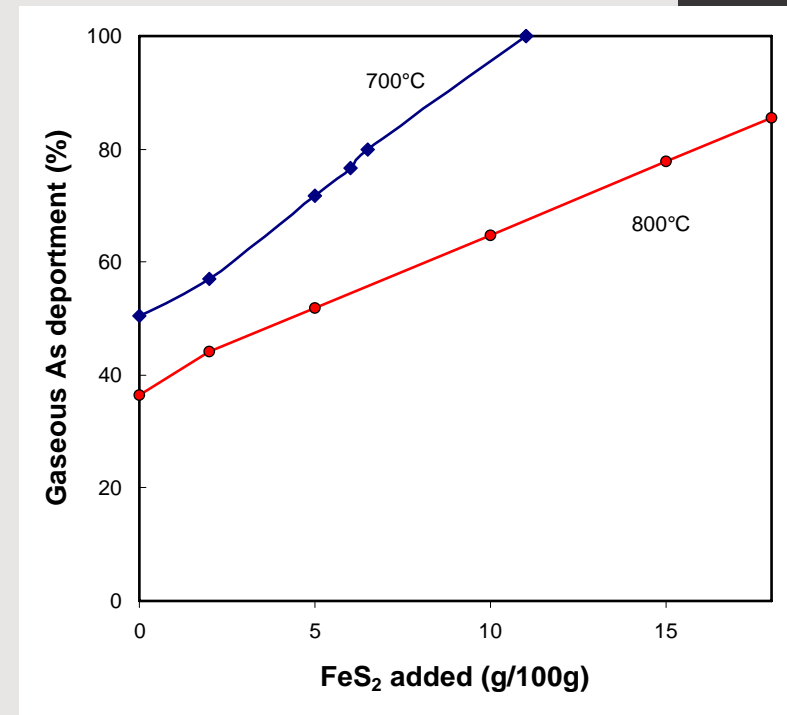
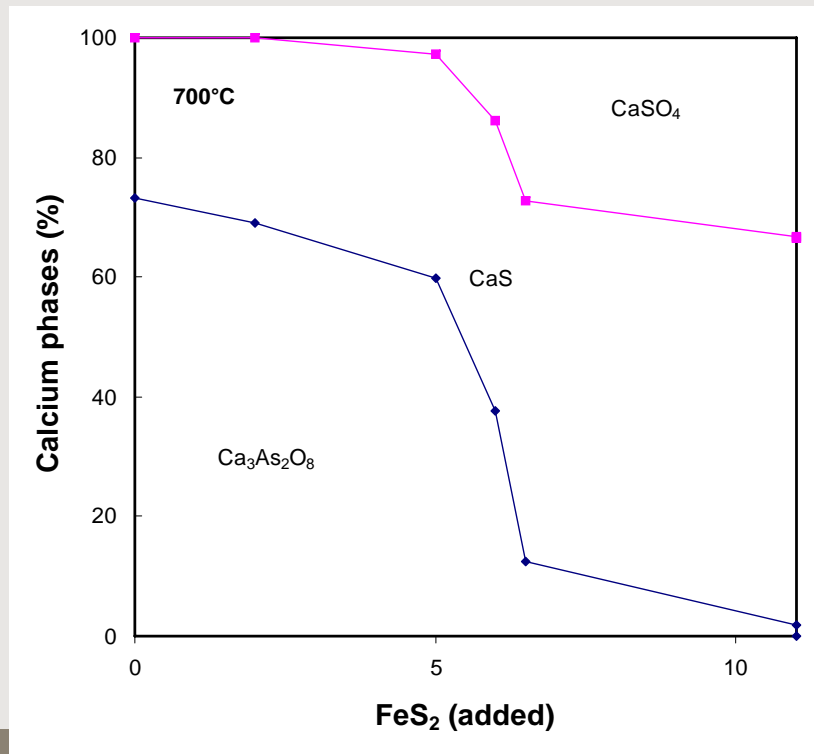


- Partial roasting with N_2/O_2 lowers As recovery
- Calcium arsenate is more stable at all temps.
 - At fixed pSO_2 , attributed to raising pO_2 and decreasing pS_2
 - Addition of sulphidant (FeS_2) should increase As recovery



Addition of Sulphidant

- FeS_2 addition increased As recovery
 - Increased $p\text{S}_2$, decreased $p\text{O}_2$
 - Decreased the stability of $\text{Ca}_3\text{As}_2\text{O}_8$
 - Increased stability of CaS



Comparison with experiments



- 60% removal of As at 700°C, 65% at 800°C
 - Conditions not identical to thermodynamic modelling
 - Greater oxidation of concentrate than modelled under neutral conditions
 - > 66% S retained, cf 95% thermodynamic prediction
 - As retained as $\text{Ca}_3\text{As}_2\text{O}_8$
- Adding pyrite increased As removal to 75%.

Conclusions



- As does volatilise from copper concentrate under neutral-slightly oxidizing conditions (low $p\text{SO}_2$)
- As_4S_4 and As_4 are the dominant volatile As species
 - Confirms the tennantite decomposition reaction
 - $\text{Cu}_{10}\text{Fe}_2\text{As}_4\text{S}_{13} = 5\text{Cu}_2\text{S} + 2\text{FeS} + \text{As}_4\text{S}_4(\text{g}) + \text{S}_2(\text{g})$
 - Decomposition temperature @ 1 atm total pressure $\sim 660^\circ\text{C}$
 - Addition of sulphidant did not decrease $p\text{As}_4\text{S}_4$
 - Increasing $p\text{SO}_2$ (decreasing $p\text{S}_2$) decreased $p\text{As}_4\text{S}_4$
- Thermodynamics controlled by $\text{CaS}/\text{Ca}_3\text{As}_2\text{O}_8/\text{CaSO}_4$
- Complete removal of As thermodynamically achievable
 - Optimum between $700\text{-}750^\circ\text{C}$ ($p\text{SO}_2$ 0.007-0.02)
 - Adding FeS_2 will also be beneficial

Opportunities



- Flowsheet for selective/early removal of As works
 - Flootation to produce 2 Cu grades –Lo As & Hi As proven at the lab/pilot scale
 - Roasting to remove As without destroying fuel value and agglomerating the concentrate
 - Thermodynamically possible
 - Experimentally confirmed - some further optimisation required
- Concept could be extended to other elements/minerals
 - As is not the only volatile element at modest roasting temperatures
 - E.g. Sb also associated with As in Tennantite
 - Possibility of segregation with As into the High As concentrate
 - Limitation on thermodynamic data to predict behaviour