2015-2016 Spring Semester Material and Energy Balance

Molybdenum

Assist. Prof. Dr. Murat Alkan

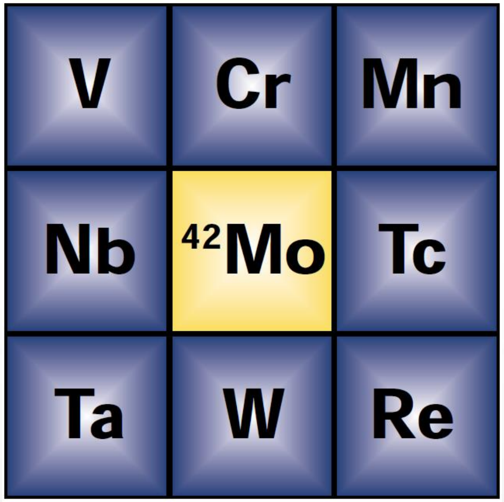
05.06.2016

Content

- Basic Info about Molybdenum
- Production Routes of Molybdenum
- Material & Energy Balance Calculations
    - Mining of Moly Ores
    - Flotation Process
    - Calcination Process
    - Leaching Process
    - Reduction Process
    - Ferromolybdenum Production

Molybdenum

- Molybdenum is a refractory metallic element used principally as an alloying agent in cast iron, steel, and superalloys to enhance hardenability, strength, toughness, and wear- and corrosion-resistance.
- Moreover, molybdenum finds significant use as a refractory metal in numerous chemical applications, including catalysts, lubricants, and pigments.



PROPERTIES

Atomic Weight:	95.95 g/g atom
Density:	10.22 g/cc
High Melting Temperature	2610°C
Lowest Thermal Expansion Coefficient of the Engineering Metals:	4.3 x 10^{-6}/°C
High Thermal Conductivity:	142 W/m•K at 20°C
Crystal Structure: Body-Centred Cubic; Lattice Constant:	a=3.1468 Å

PRIMARY CONSUMPTION SECTORS BY END-USE*

Stainless Steels & Super Alloys	30%
Low Alloy Steels	30%
Chemicals & Mo Metal	20%
Tool & High Speed Steels	10%
Foundry	10%
* IMOA estimates	

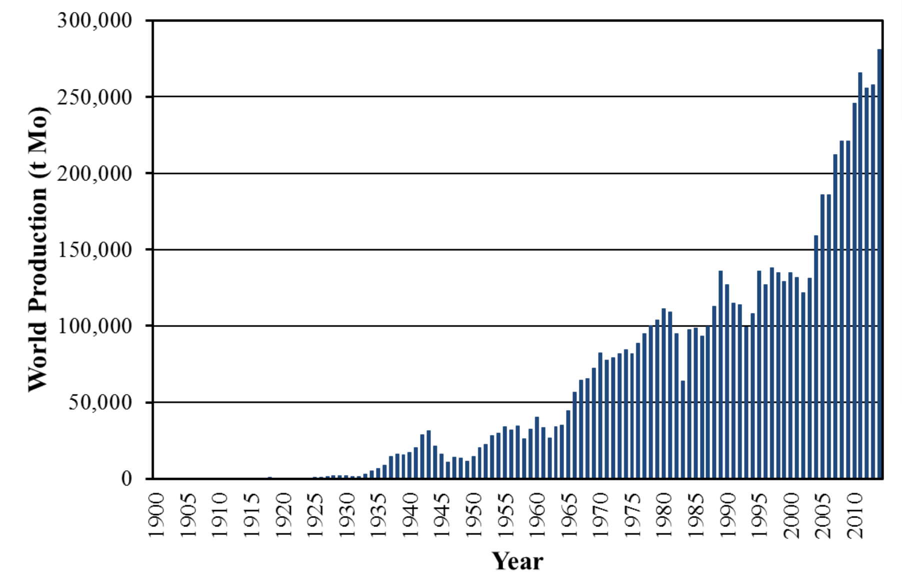
Source: Molybdenum, 1998, IMOA, webpage.

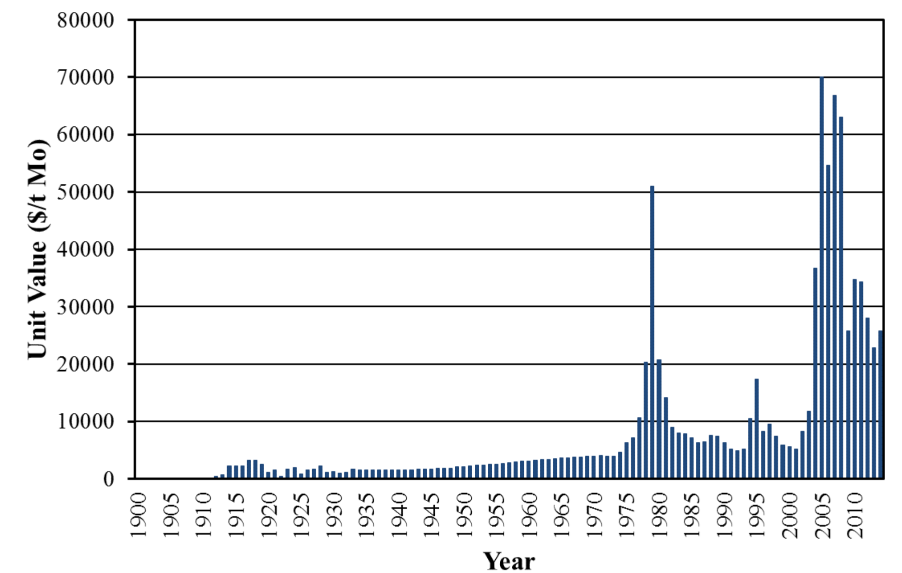
Molybdenum Minerals and Deposits

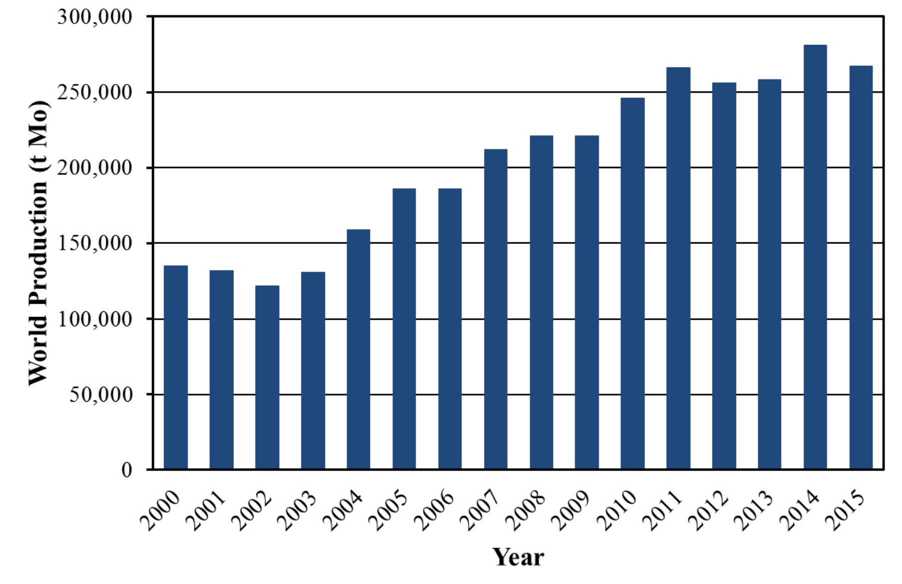
- Molybdenum occurs in the earth's crust in an abundance of about 10^{-4} %, mainly as molybdenite (MoS_2). Wulfenite ($PbMoO_4$), powellite [$Ca(Mo,W)O_4$], Ferrimolybdite ($Fe_2Mo_3O_{12}\cdot 8H_2O$) are the other significant minerals. There are five genetic types of molybdenum deposits:
  - 1) porphyry deposits in which metallic sulfides are disseminated throughout large volumes of altered and fractured rock,
  - 2) contact-metamorphic zones and bodies in which silicated limestone is adjacent to intrusive granites,
  - 3) quartz veins,
  - 4) pegmatites, and
  - 5) deposits bedded in sedimentary rocks.
- Average molybdenite concentrations in primary porphyry deposits range from 0.05 to 0.25 %; in secondary copper – molybdenum porphyry deposits molybdenite concentrations are much lower (0.01 – 0.05 %) so that the mineral can only be recovered as a byproduct.

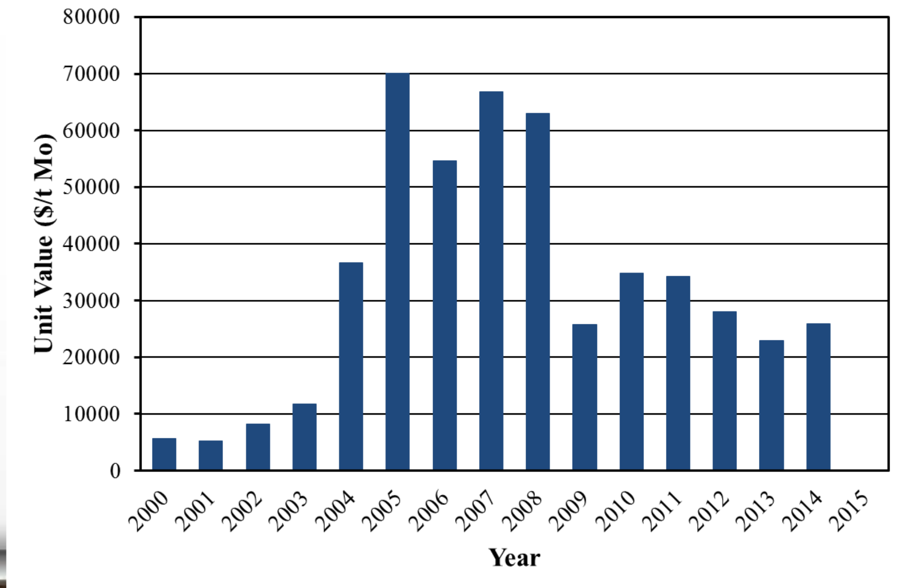
Source: A.R.Burkin, 2005, Molybdenum and Molybdenum compounds, in Ullmann's…

Molybdenum Mine Production and Prices



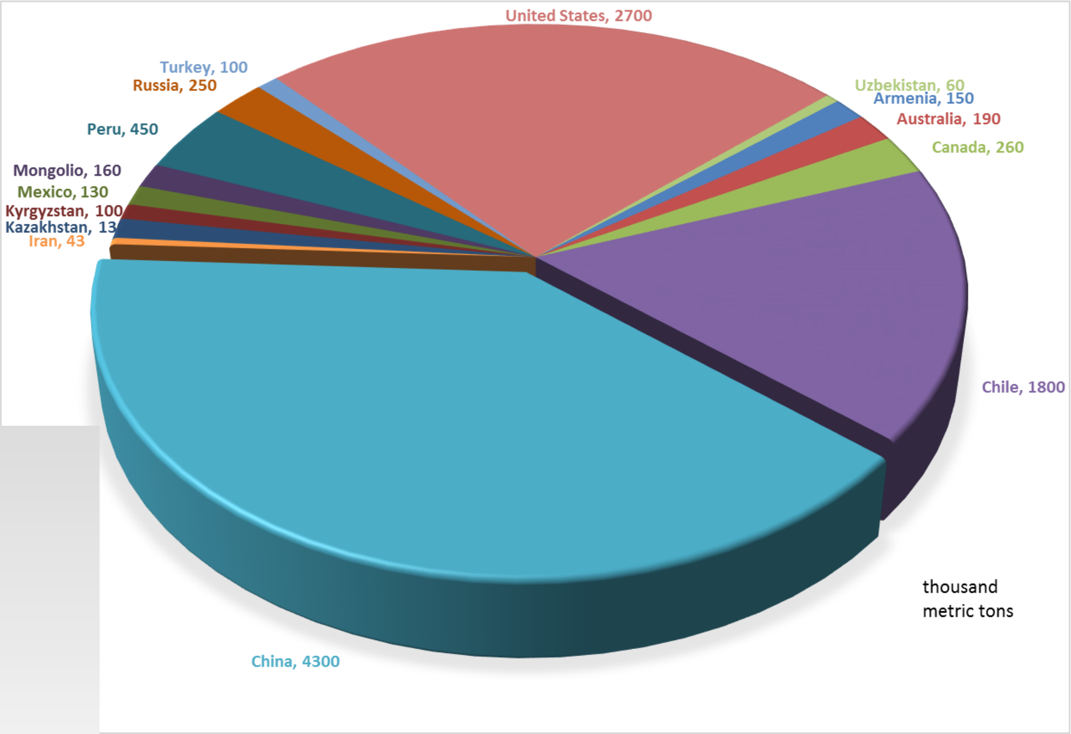


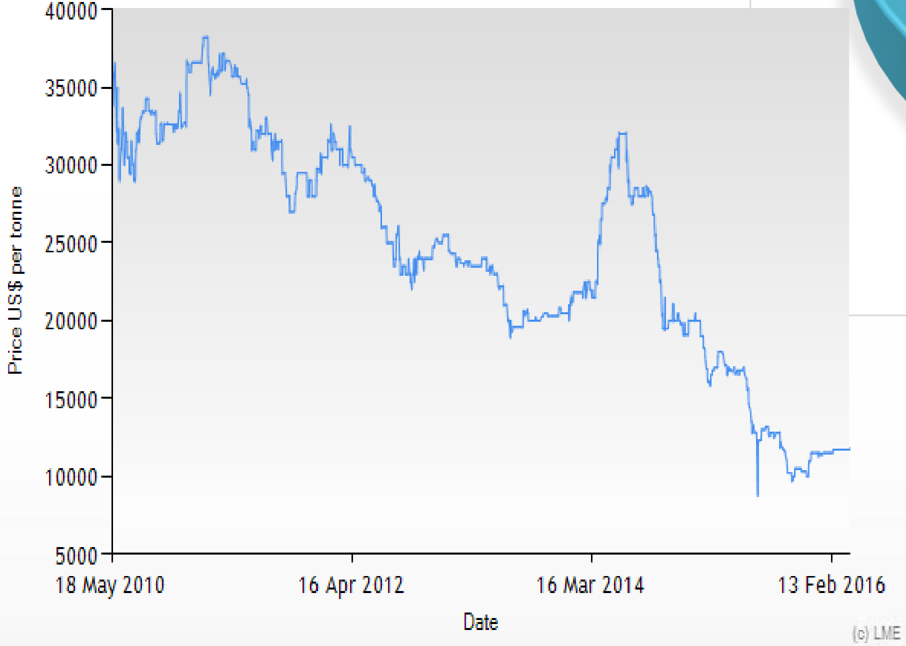




Source: D.E. Polyak, 2016, Molybdenum Statistics, USGS.

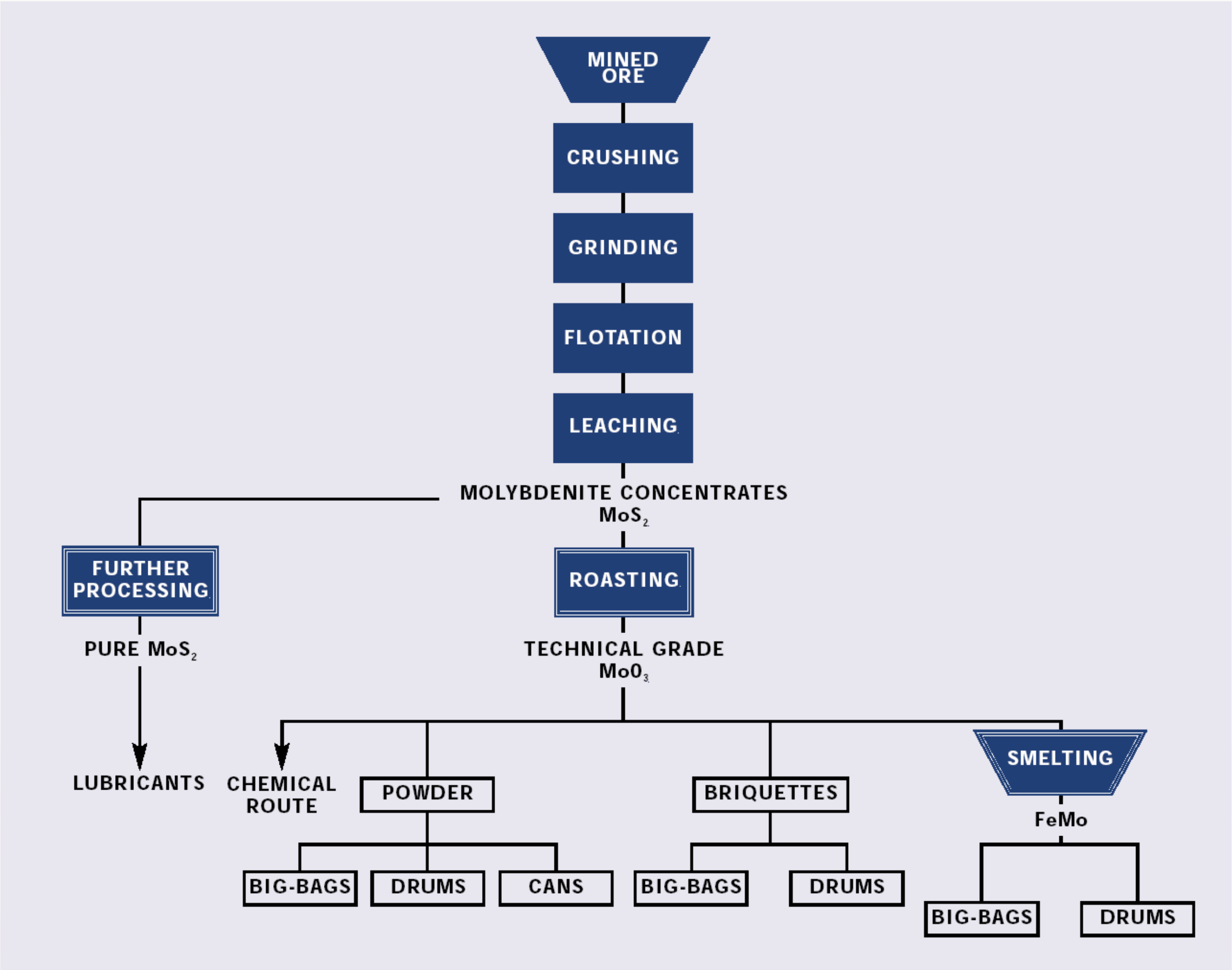
Molybdenum Reserves and Prices





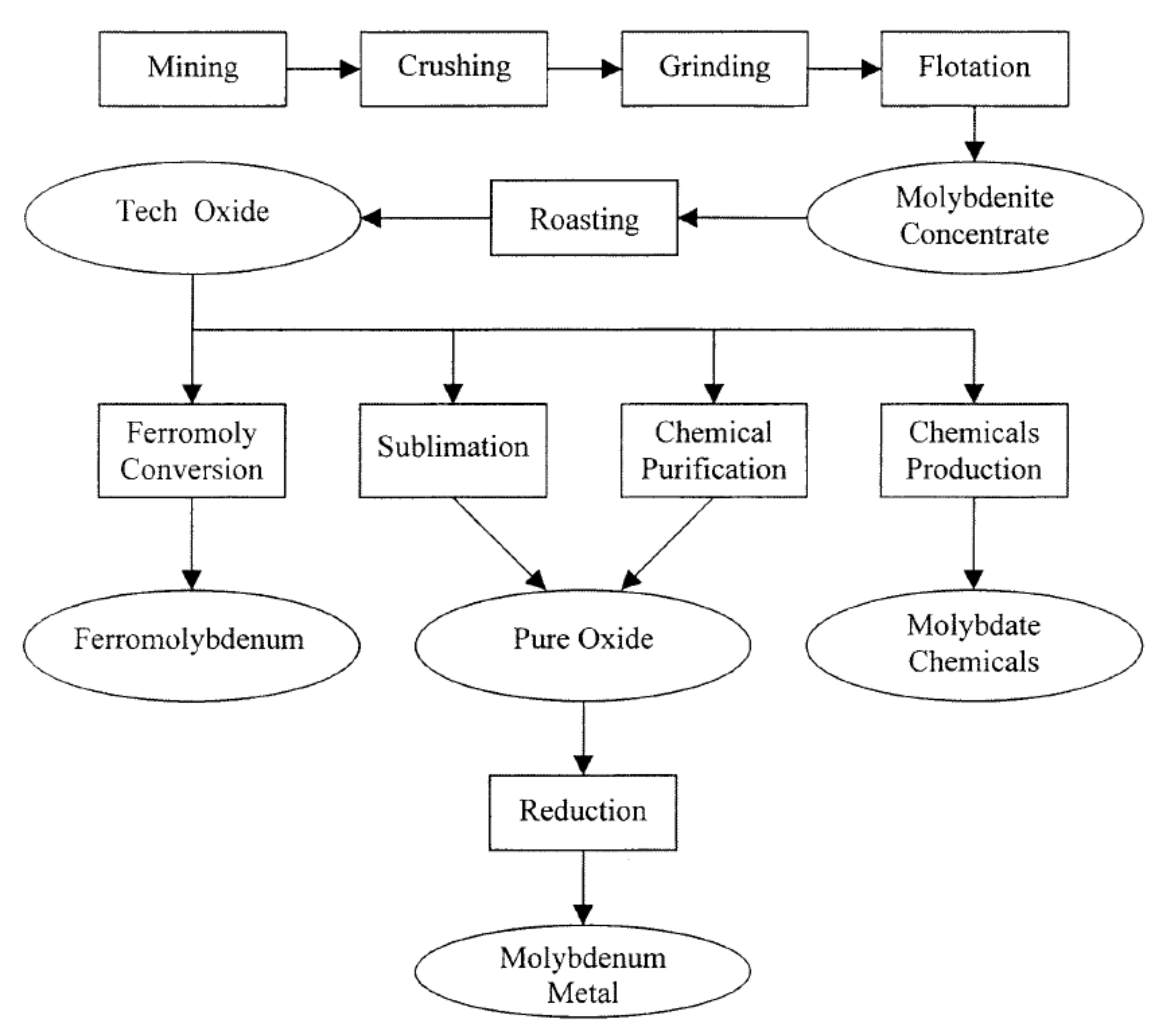
Sources: D.E. Polyak, 2016, Molybdenum Statistics, USGS. LME.com, 2016

Molybdenum Production Route



Source: Molybdenum, 1998, IMOA, webpage.

Molybdenum Production Route



Source: M.C. Jha, 2001. Extractive Metallurgy of Molybdenum, TMS2001

M.&E.B. Calculations in Moly Mining

- Molybdenum ore is mined by underground and open-pit methods.
- A typical primary molybdenum ore body contains 0.05 – 0.25% Mo,
- and secondary ore bodies (copper porphyry ores) average 0.3 – 1.6% Cu and 0.01 – 0.05% Mo.

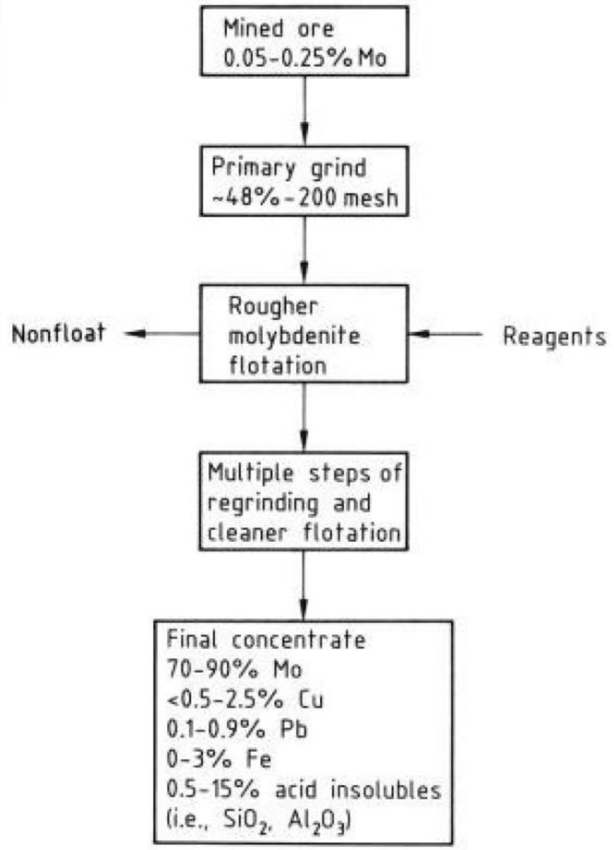


Figure 1. Primary molybdenite recovery process [9]

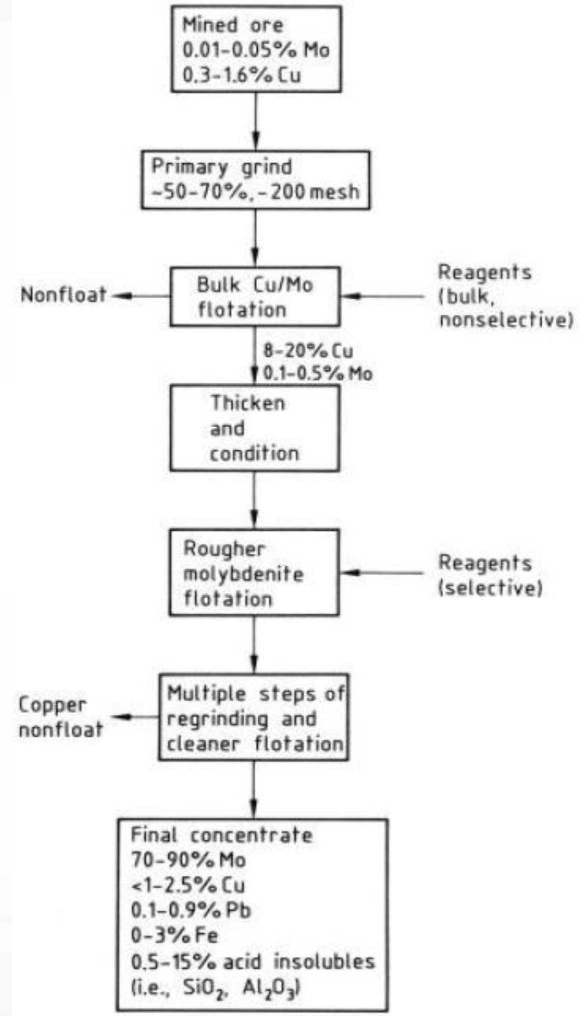


Figure 2. Byproduct copper–molybdenite recovery process [9]

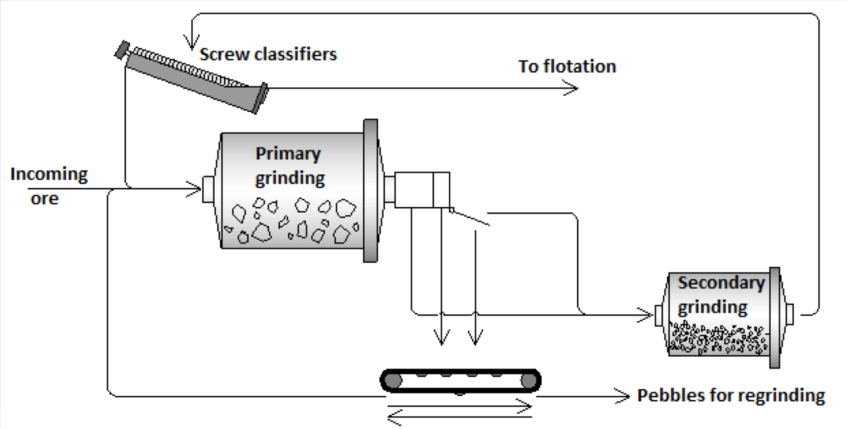
Source: A.R.Burkin, 2005, Molybdenum and Molybdenum compounds, in Ullmann's…

Mining

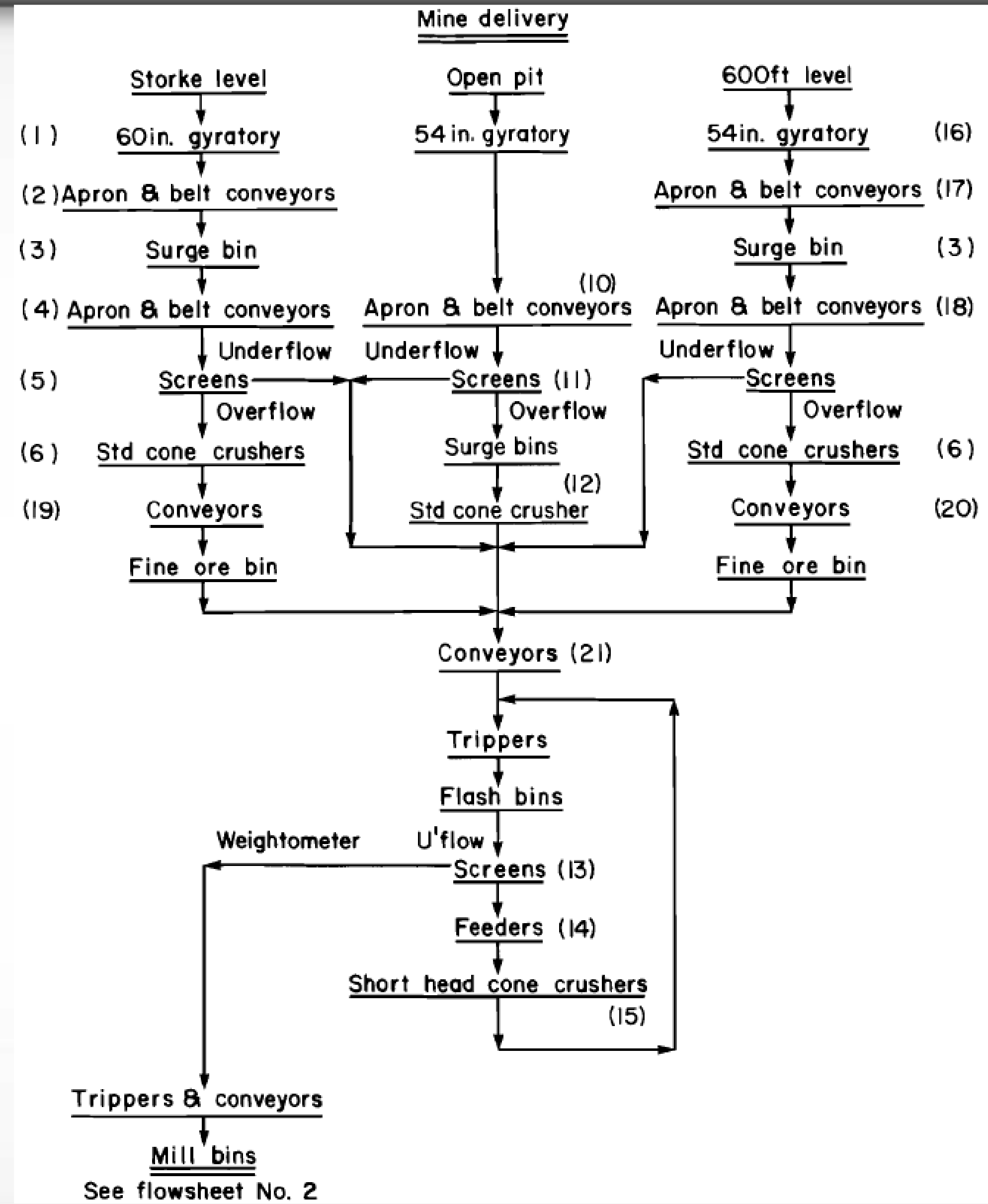
- Let assume that we have a primary molybdenum ore with the mass composition of 40% quartz (SiO_2), 20% orthoclase ($KAlSi_3O_8$), 15% plagloclase ($NaAlSiO_3O_8$), 5% Mica-sericite ($Na_2O.K_2O.3Al_2O_3.6SiO_2.2H_2O$), 5% Clay ($4SiO_2.3MgO.H_2O$), 5% Pyrite ($FeS_2$), 2% Fluorite ($CaF_2$), 1% Topaz ($Al_2SiO_4(F,OH)_2$), 0.35% MoS_2, 0.02% Chalcopyrite ($CuFeS_2$).
- This is an example of Climax-Porphyries deposits. We can design similar mining facility like in Climax Mine, Colorado.

Source: C.K. Gupta, Extractive Metallurgy of Molybdenum

Mining



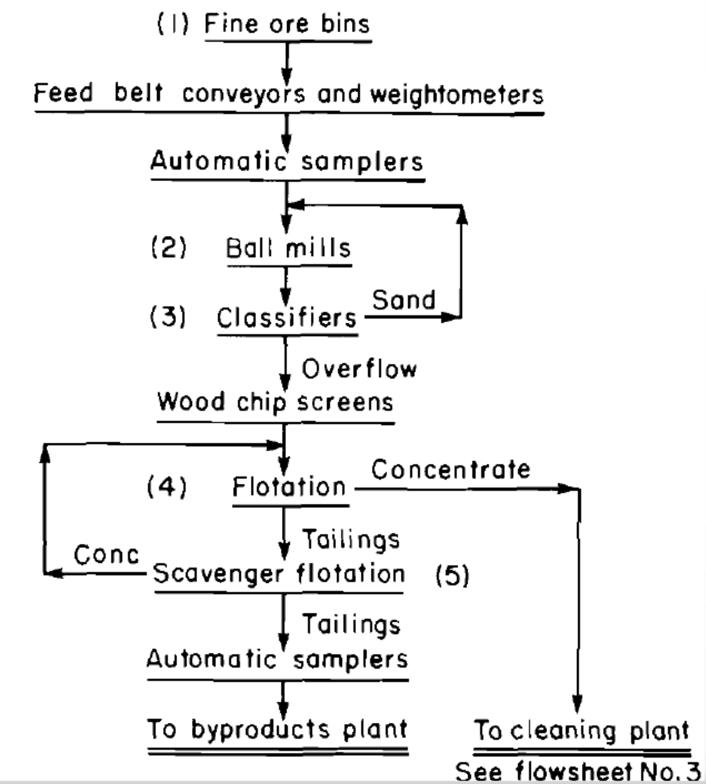
- For mining calculations, energy is required during transportation, milling, grinding, screening, feeding applications. Material balance calculations will be applied in screening and classification sectors.

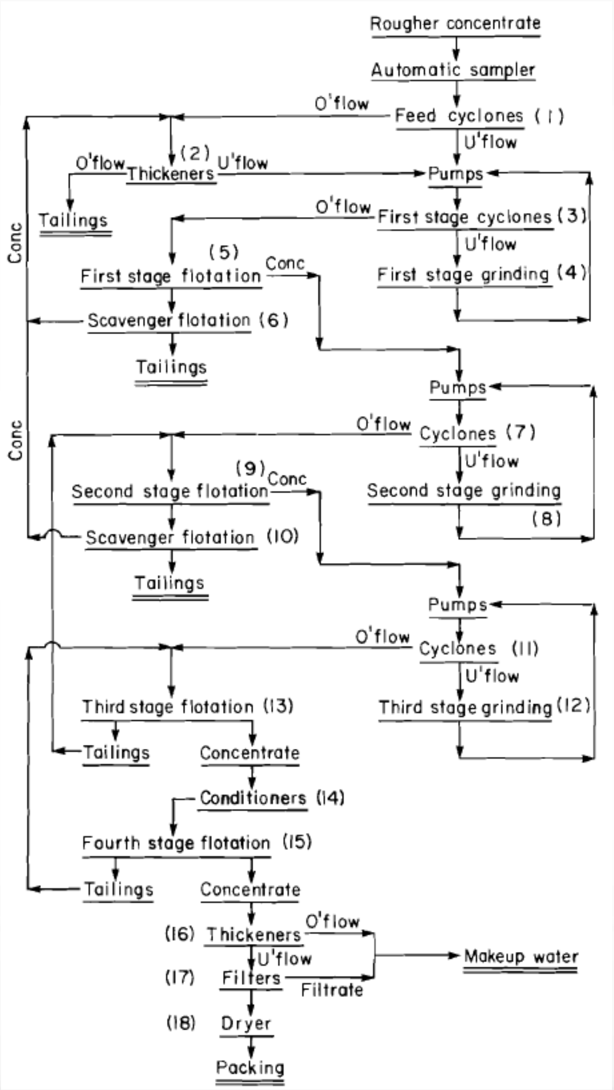


Source: …

M.&E.B. Calculations in Moly Flotation

- After grinding, classifier overflow is pumped to flotation step. Froth flotation step realized in two steps: Rougher flotation, cleaner flotation.





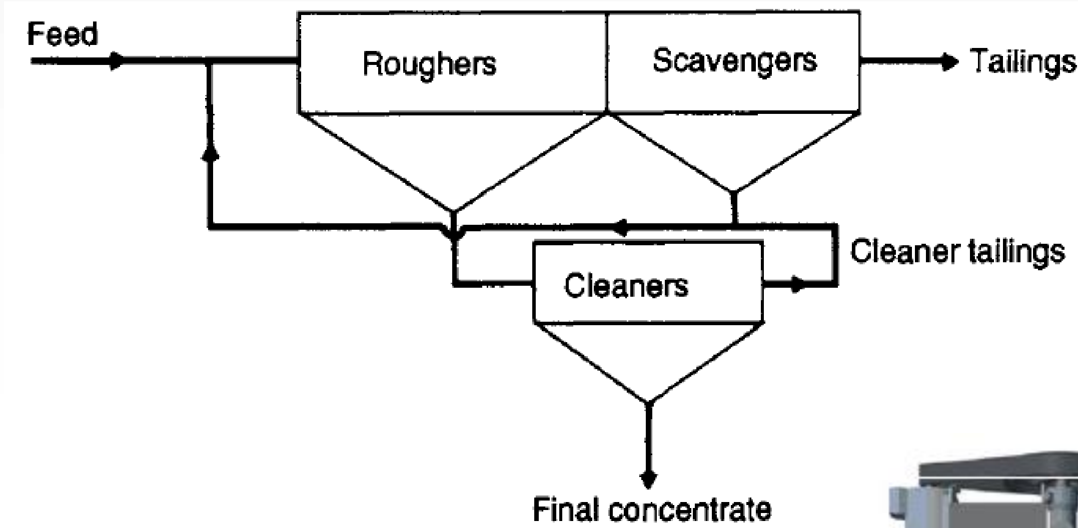
Source: JD Vincent and JF Shirley, 1978, Molybdenum,

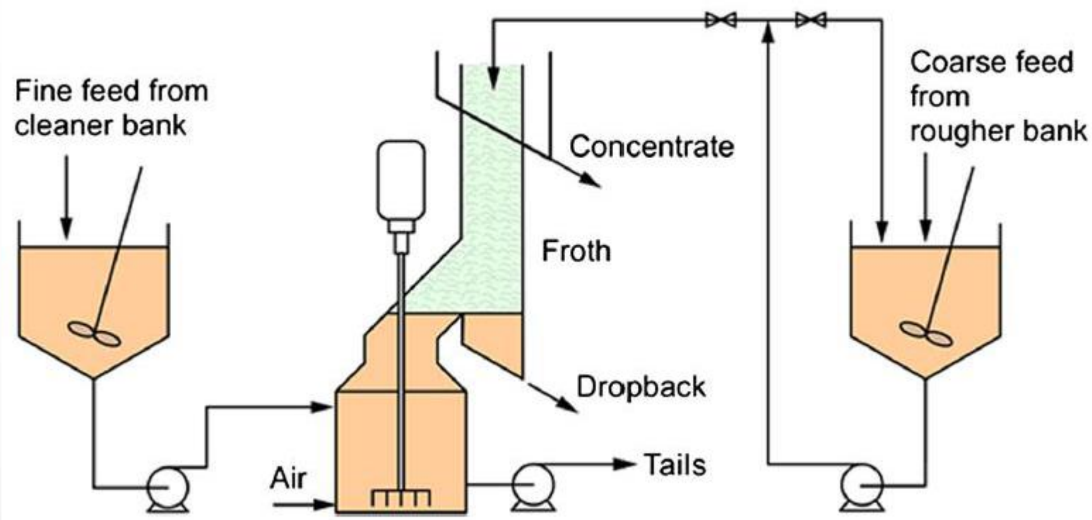
Rougher Flotation Calculations

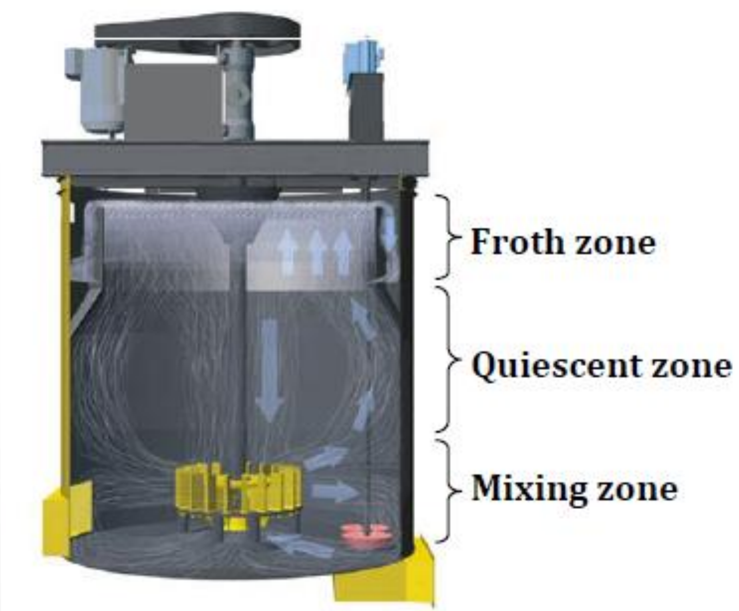
- We have molybdenum ores with 0.35 wt.% MoS_2, and we have a daily feed of 50,000 tons of ores.
- Water consumption is 600 gallon per ton of feed.
- Flotation reagents are added to the system for per ton of ore as; 0.035 lb pine oil, 0.67 lb vapor oil, 0.034 lb Syntex, 0.30 lb lime, 0.50 lb sodium silicate, 0.03 lb nokes reagent.
- Rougher concentrate has 5.5 wt.% MoS_2, and overall MoS_2 recovery is 87%.
- The ratio of water in concentration is 350 to 1.
- Rough flotation process takes place 15 minutes for each cell.

Source: JD Vincent and JF Shirley, 1978, Molybdenum

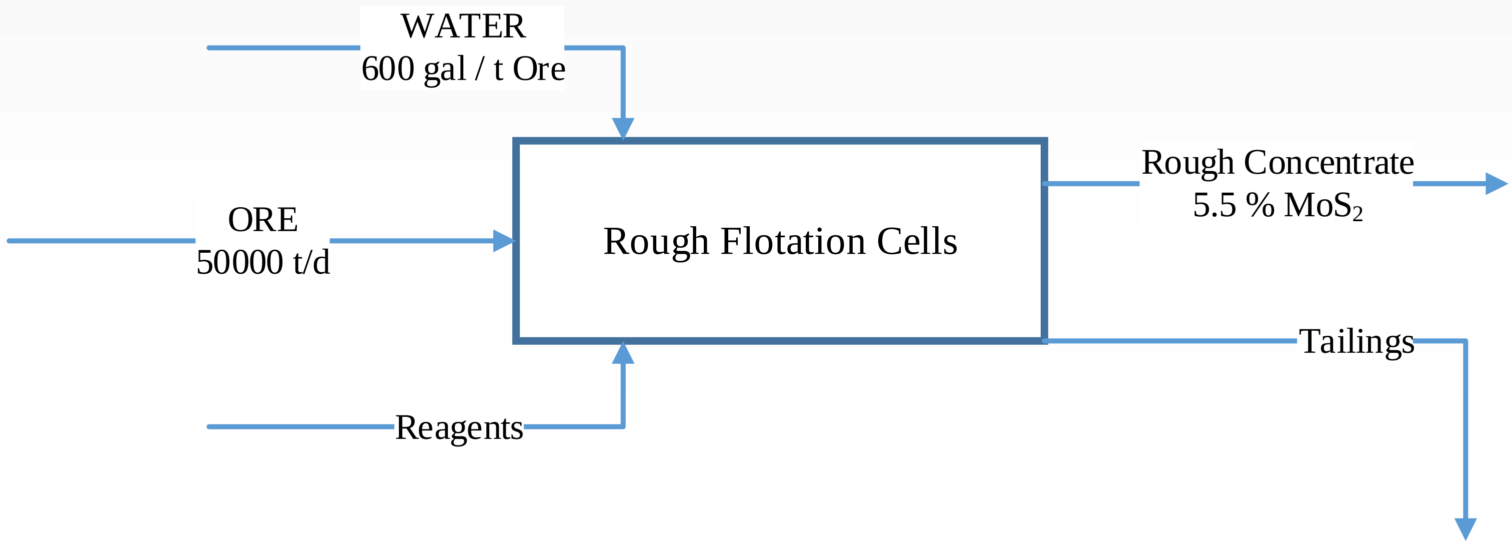
Rougher Flotation Calculations





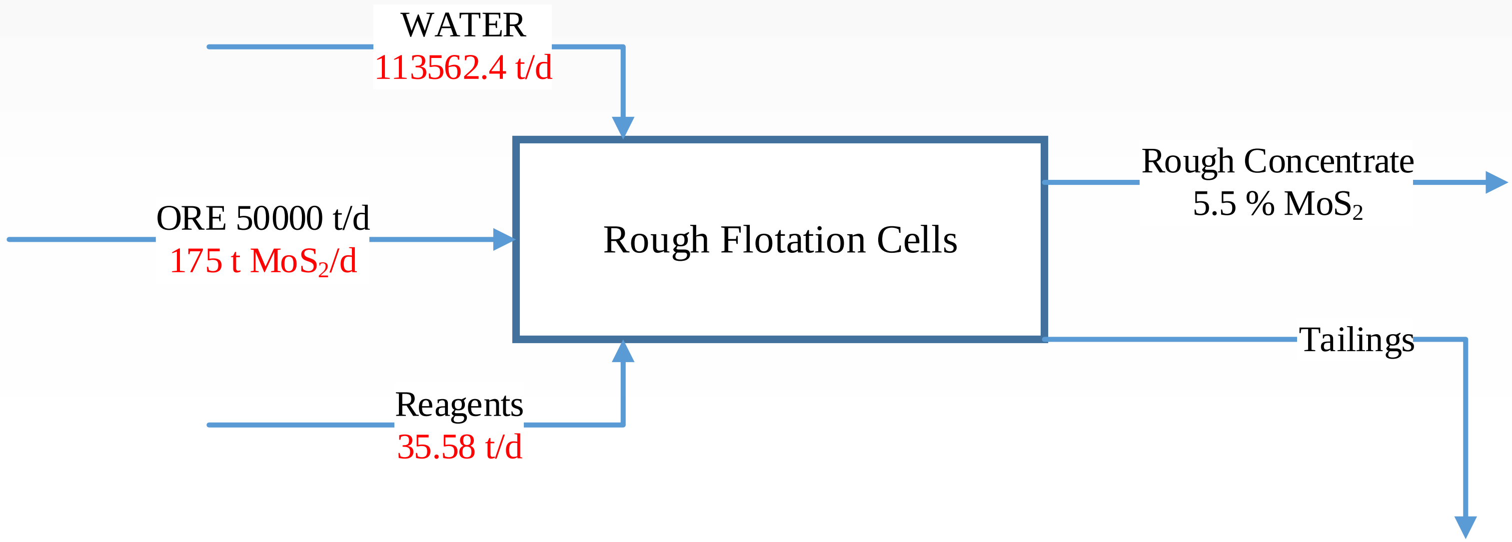


Material Balance



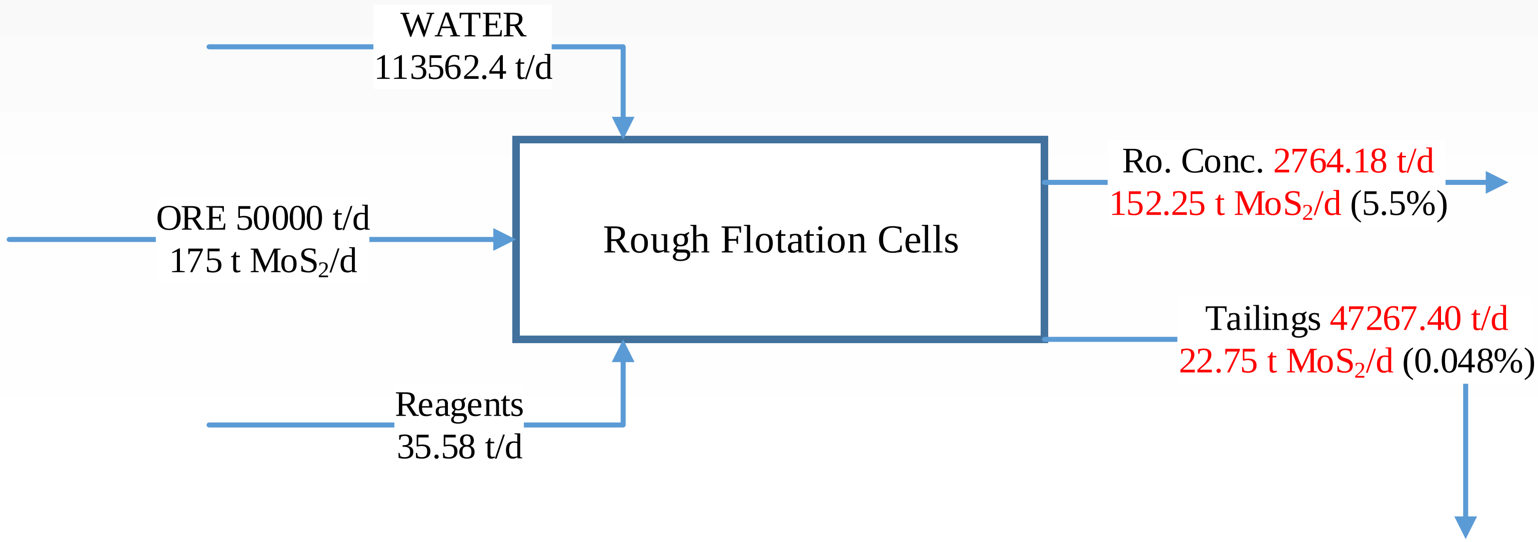
- 50000 t/d ores contain 50000x0.35% = 175 t MoS_2 /d
- 50000 t/d ores require; v_{water}=50000x600 =$3x10^7$gal=113562.4 m^3
- d_{water}=1000kg/m^3 so m_{water}=113562.4 t/d
- Amount of reagents are; 0.79 t/d pine oil, 15.20 t/d vapor oil, 0.77 t/d Syntex, 6.80 t/d CaO, 11.34 t/d Na_2SiO_3, 0.68 t/d $Na_3PS_2O_2$. Total 35.58 t/d reagents.

Material Balance



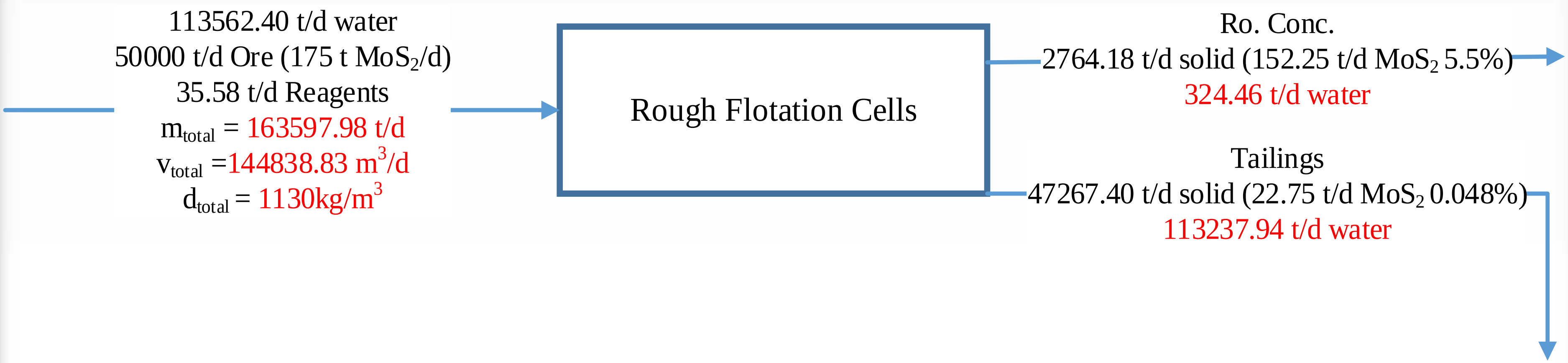
- Flotation process has 87% efficiency. So,
- 175x0.87=152.25 t MoS_2/d recovered into concentrate
- 175-152.25=22.75 t MoS_2/d go into tailings.
- Concentration has 5.5 wt.% MoS_2. So;
- $m_{conc.}$=152.25/(5.5%)=2768.18 t/d
- $m_{tail.}$=50035.58-2768.18=47267.40 t/d (0.048 % MoS_2)

Material Balance



- Amount of water is 113562.4 t/d. Concentration has 350 to 1 ratio. So,
- $m_{\text{water in conc.}}$ = 113562.4/350=324.46 t/d
- $m_{\text{water in tail.}}$=113237.94 t/d
- Total weight of the raw material = 163597.98 t/d
- Total volume of the raw materials = 144838.83 m^3/d (calculated from density values of raw material)

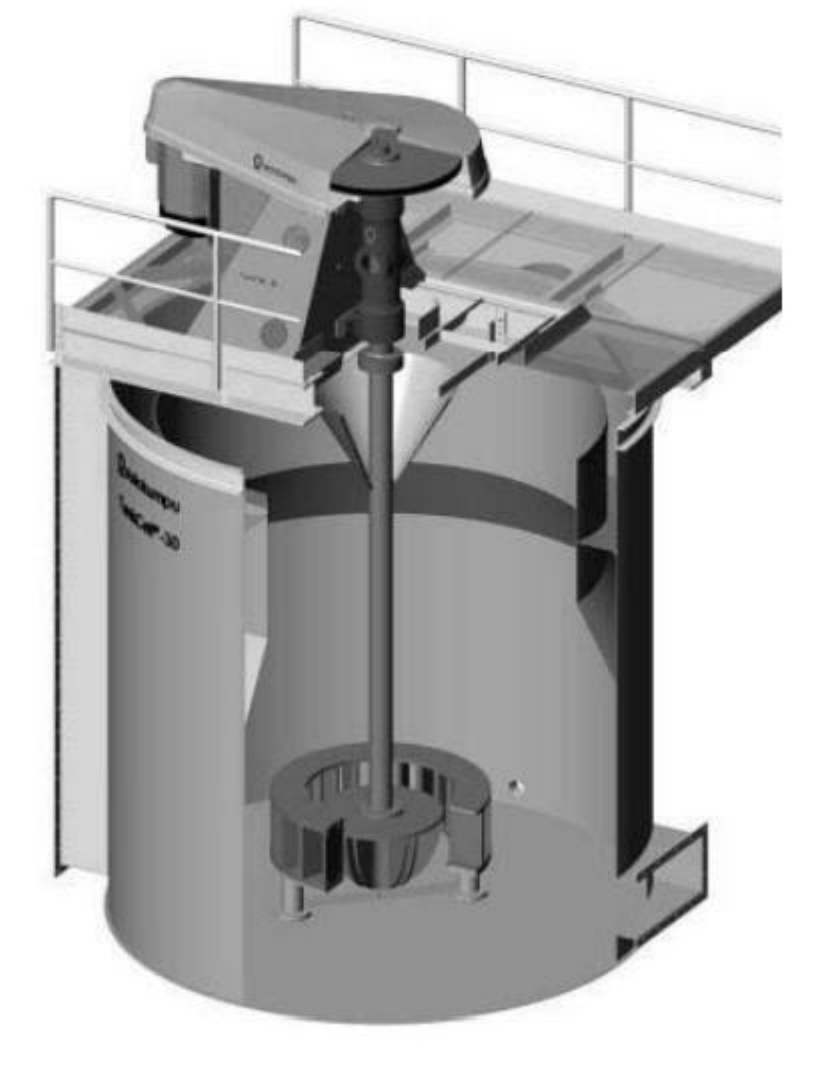
Material Balance



- Total volume of the raw material is 144838.83 m^3/d. Flotation time is 15 min. So, in a single day (24x60)/15=96 cycle applied.
- 144838.83 / 96 = 1508.73 m^3 per flotation cycle. We need at least 1600 m^3 total flotation capacity plant.

Energy Balance

- There is no heating and cooling require for this process, and there is no reaction. We need energy during flotation and pumping.
- Let's select flotation cell from Outokumpu TankCell. We need at least 1600 m^3 total flotation capacity plant.
- For OK-100-TC type flotation cell (with 100 m^3 volume) a 110 kW capacity motor is used.
- In 16 cells, 110x16x24=42240 kWh energy consumed per day for rough flotation.

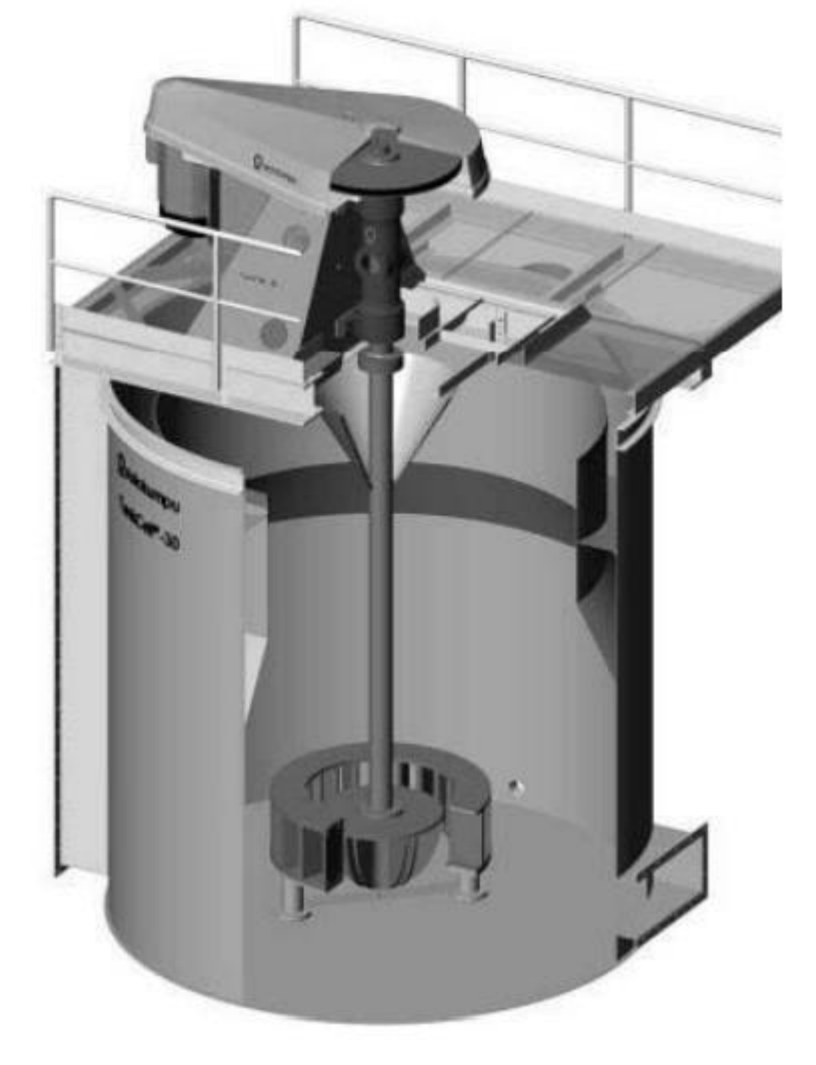


A schematic diagram of Outokumpu TankCell

Source: B.K. Gorain, 2000. Flotation Cell Design: Application of Fundamental Principles

Energy Balance

- We also require energy for hydrodynamic process. For 87% Mo recovery, we obtain
  - 0.84 kW/m^3 specific power for pumping,
  - 195 m^3/min pumping rate,
  - 34.0 m^3/min airflow.
- 1600m^3x0.84x24=32256 kWh energy
- 34x24x60=48960m^3 air consumed.
- Total 32256+42240=74496kWh energy consumed per day for rough flotation

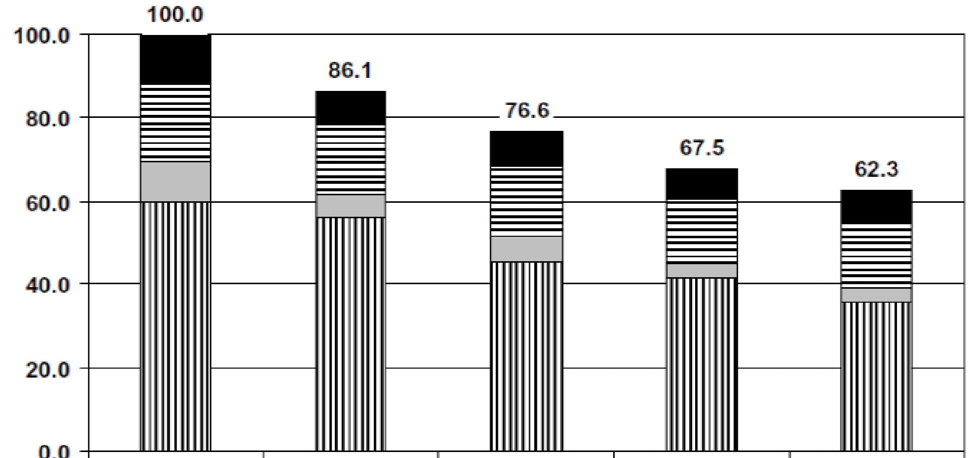


A schematic diagram of Outokumpu TankCell

Source: D.Lenindski, 2011, Effective use of energy in the flotation process

Energy Balance

- This is a comparison of
  - 18 cells of 100 m^3 in two lines of nine cells.
  - 9 cells of 200 m^3 in a single line.
  - 9 cells of 200 m^3 in a single line, fitted with variable speed drive mechanisms.
  - 6 cells of 300 m^3 in a single line.
  - 6 cells of 300 m^3 in a single line, fitted with variable speed drive mechanisms.

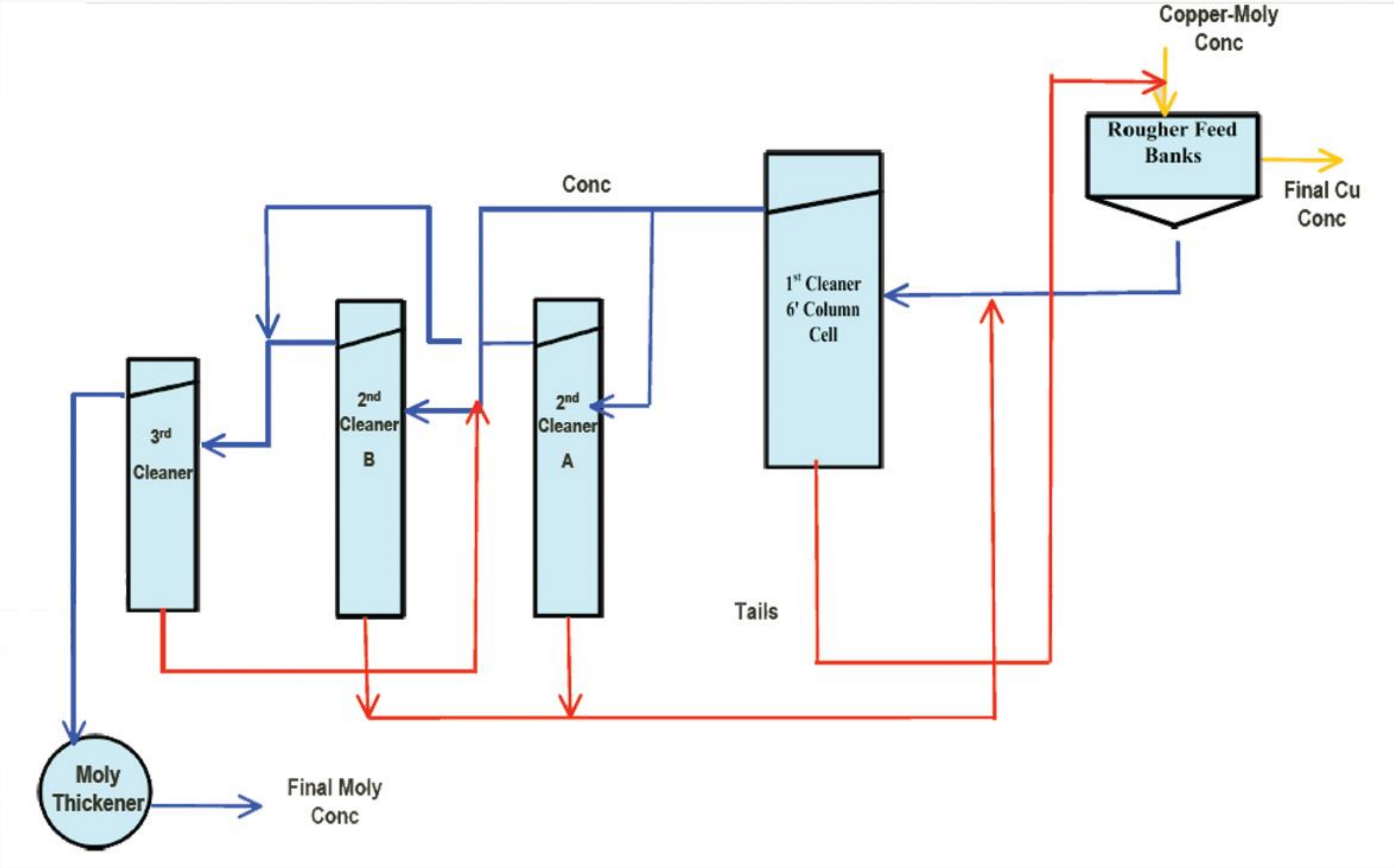


	100-m3 cells	200-m3 cells	200-m3 cells, optimized rotation speed	300-m3 cells	300-m3 cells, optimized rotation speed
Investment costs	11.9	7.4	8.2	7.0	7.7
Reagents	18.7	17.0	17.0	15.4	15.4
Maintenance	9.4	5.8	6.0	3.5	3.6
Energy	60.0	55.9	45.4	41.5	35.6
LCC	100.0	86.1	76.6	67.5	62.3

- If we use 300m^3 rather than 100m^3 cell, we could save;
- 74496x(60-41.5)/60=22969.9 kWh per day

Source: C.R. Boeree, 2014, Up-scaling of froth flotation equipment.

Cleaner Flotation Calculations



Similar calculations can be also made for cleaner flotation step.

Source: R.Rogers, 2010, Design, installation and operation of Pinto Valley moly flotation.

Cleaner Flotation Calculations

Mass balance of the new moly plant configuration.

	Solids			Water, GPM		Pulp
Stream	% MoS_2	DTPD	% Solids	Drip pan	Launder	GPM
Ro feed	1.6	953.7	26.0			489.6
Ro tails	0.4	883.1	27.1			430.4
Ro conc	17.4	70.7	17.7		15	57.5
First cleaner Feed (6' col.)	15.2	102.1	12.0			283.4
First cleaner Tail (6' col.)	9.0	62.0	14.0	10		212.6
First cleaner Con(6' col.)	25.0	39.5	10.0		10	70.8
Second cleaner Feed (30" col.)	34.7	72.1	8.0			111.3
Second cleaner Tail (30" col.)	9.0	31.4	6.5	10		78.7
Second cleaner Con (30" col.)	60.0	40.6	18.0		10	32.9
Third cleaner Tail (20" col.)	50.0	34.9	16.5	5		20.4
Third cleaner Final con (20" col.)	90.0	5.7	35.0		5	12.5
Scavenger cail (30" col.)	6.0	53.7	4.0	10		160.4
Scavenger con (30' col.)	25.0	9.6	3		10	62.2

Design parameters of the flotation columns.

Flotation column parameter	Scavenger	Second cleaner	Third cleaner
Height (h), ft	32	32	25
Diameter (d), in.	30	30	20
h/d, ft/ft	12	12	15
Flow feed, gpm	220	120	35
Nitrogen, scfm	10	10	5
Nitrogen, psi	50	50	50
hold up, %	15	15	12
Feed superficial velocity, cm/s	1.5	1.5	1.2
Water superficial velocity, cm/s	0.122	0.122	0.108
Froth depth, in.	12	12	9

Source: R.Rogers, 2010, Design, installation and operation of Pinto Valley moly flotation.

Cleaner Flotation Calculations

- Molybdenite ore with 0,05 – 0,25 % Mo milled and grinded to 74 µm.
- Gravitation, agitating with water, collecter oil and other chemicals.
- Flotation with kerosene, stove oil, light oil, pine oil, Syntex VB (sulfated monoglyceride of coconut oil) and lime or soda ash for alkalinity for pH 8,5. Sodium silicate is used to disperse slimes.
- 70-90 % MoS_2 with 0,5-2,5 % Cu, 0,1-0,9 % Pb, 0-3 % Fe.

Source: A.R.Burkin, 2005, Molybdenum and Molybdenum compounds, in Ullmann's…

Roasting of Molybdenum Concentrate

- Molybdenite concentrates are convened to technical grade oxide, which is the starting material for a variety of products for the metallurgical and chemical industries.
- The roasted concentrate is discharged from the furnace and either marketed as technical grade oxide or subjected to additional conversion operations to remove impurities.

Typical concentrations in the analysis range of molybdenite concentrates are:

	Wt %
Total molybdenum	40 –59
Sulfur	34.4 –37.6
Acid insol.	1.6 –15.0
Lead	0.002– 0.03
Tin	0.003– 0.006
Zinc	0.002– 0.02
Bismuth	0.006– 0.09
Phosphorus	0.002– 0.04
Iron	0.3 – 1.0
Copper	0.006– 2.0
Oil	0.5 – 8.3
Water	0.5 – 8.4

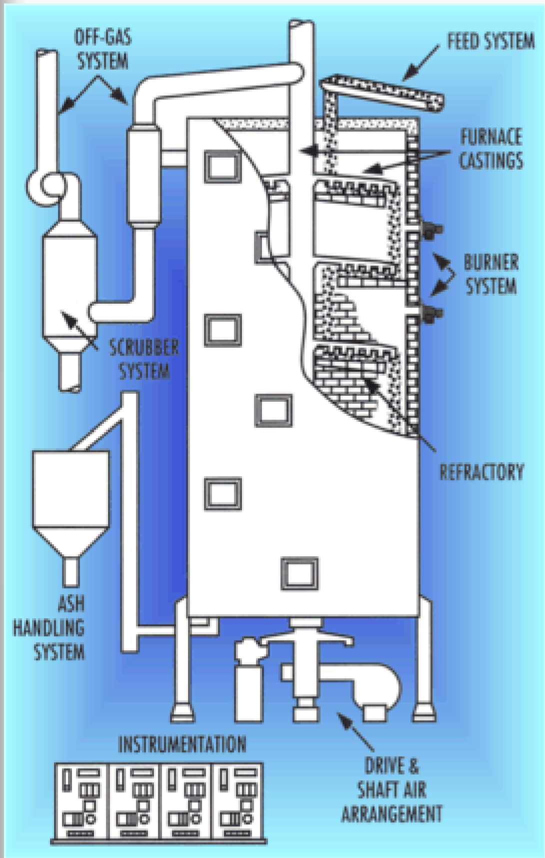
$$MoS_2 + \frac{7}{2} O_2 \rightarrow MoO_3 + 2SO_2.$$

A typical analysis range of commercially available technical grade molybdic oxide is:

	Wt %
Molybdenum	56 –62
Sulfur	0.02 – 0.25
Insolubles	5.00 –11.00
Iron	0.50 – 1.00
Copper	0.015– 1.00
CaO	0.05 – 0.20
ZnO	0.10 – 0.20

Source: …

Roasting of Molybdenum Concentrate



$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$$

$$MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2$$

$$2MoO_2 + O_2 \rightarrow 2MoO_3$$

- Molybdenite is converted to technical-grade MoO_3 by roasting it in air in a multiple hearth furnace of the Nichols-Herreshoff design.
- Upper hearth temp 600-700°C, the hearth temperatures are controlled 600-650 °C by addition of excess hot air or water sprey cooling.
- Technical-grade MoO_3 typically contains 85-90% MoO_3, the balance being silica with some Fe_2O_3 and Al_2O_3.

Source: A.R.Burkin, 2005, Molybdenum and Molybdenum compounds, in Ullmann's…

Material & Energy Balance

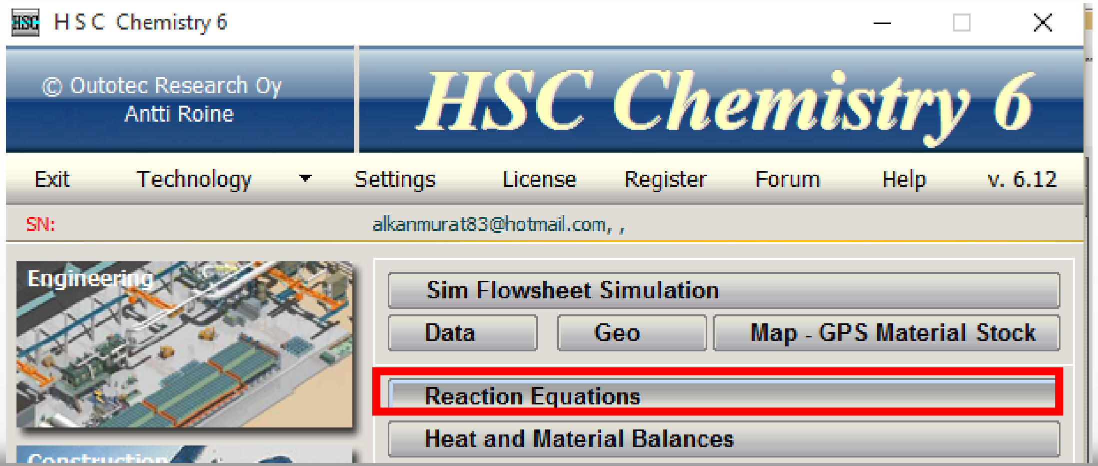
- Calcination takes place due to three reactions.

$$2\,MoS_2 + 7\,O_2 = 2\,MoO_3 + 4\,SO_2$$

$$MoS_2 + 3\,O_2 = MoO_2 + 2\,SO_2$$

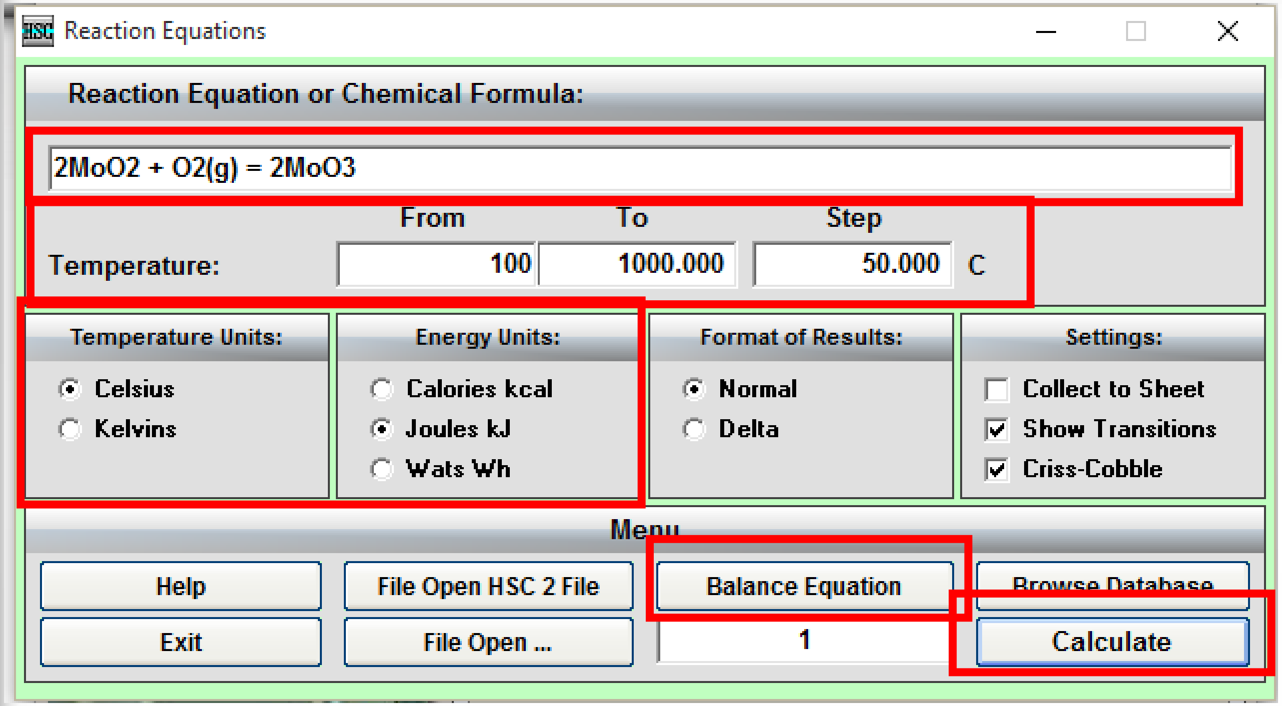
$$2\,MoO_2 + O_2 = 2\,MoO_3$$

- To decide which one is favorable, we need to plot Gibbs Free Energy Changing vs Temperature diagram (Ellingham).
- We can use "Reaction Equation" Module of HSC for obtaining data.



Source: A.R.Burkin, 2005, Molybdenum and Molybdenum compounds, in Ullmann's...

Material & Energy Balance



1- Writing the equation

!!! Attention !!!

If the phase is gaseous form write (g)

If the phase is liquid form write (l)

If the phase is in aqueous form write (aq)

2 – Temperature range and step

You can select temperature and energy unit from here

3 – Balance the equation

4 – Press Calculate for calculating

Material & Energy Balance

Results

File Edit Format Help

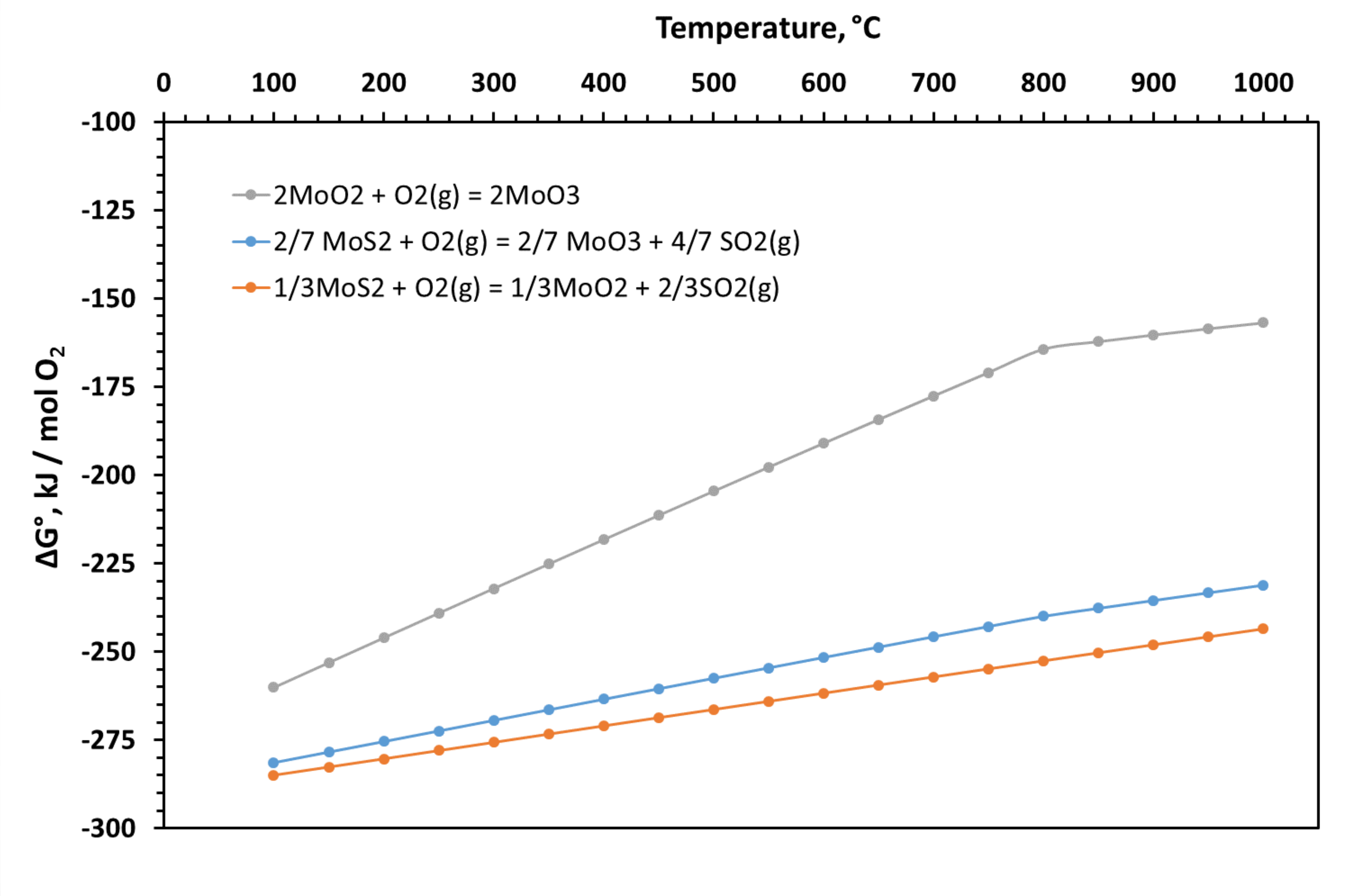
	T	Cp	H	S	G	Reference
1	2MoO2 + O2(g) = 2MoO3					
2	T	deltaH	deltaS	deltaG	K	Log(K)
3	C	kJ	J/K	kJ		
4	100.000	-312.890	-141.309	-260.160	2.637E+036	36.421
5	150.000	-312.638	-140.676	-253.111	1.767E+031	31.247
6	200.000	-312.395	-140.133	-246.091	1.480E+027	27.170
7	250.000	-312.130	-139.601	-239.098	7.500E+023	23.875
8	300.000	-311.826	-139.046	-232.132	1.437E+021	21.157
9	350.000	-311.471	-138.452	-225.194	7.553E+018	18.878
10	400.000	-311.057	-137.814	-218.287	8.708E+016	16.940
11	450.000	-310.580	-137.132	-211.413	1.871E+015	15.272
12	500.000	-310.037	-136.407	-204.575	6.643E+013	13.822
13	550.000	-309.427	-135.642	-197.773	3.558E+012	12.551
14	600.000	-308.749	-134.843	-191.011	2.678E+011	11.428
15	650.000	-308.004	-134.013	-184.289	2.682E+010	10.429
16	700.000	-307.193	-133.158	-177.610	3.421E+009	9.534
17	750.000	-306.318	-132.281	-170.974	5.363E+008	8.729
18	800.000	-305.381	-131.388	-164.382	1.004E+008	8.002
19	850.000	-205.466	-38.494	-162.231	3.512E+007	7.546
20	900.000	-203.013	-36.357	-160.361	1.383E+007	7.141
21	950.000	-200.687	-34.415	-158.593	5.933E+006	6.773
22	1000.000	-198.490	-32.654	-156.917	2.745E+006	6.438
23						
24	Formula	FM	Conc.	Amount	Amount	Volume
25		g/mol	wt-%	mol	g	l or ml
26	MoO2	127.939	88.885	2.000	255.878	39.548 ml
27	O2(g)	31.999	11.115	1.000	31.999	22.414 l
28		g/mol	wt-%	mol	g	l or ml
29	MoO3	143.938	100.000	2.000	287.876	61.355 ml
30						

Exit Help Print Clear Copy All Copy Save

- Results give us Enthalpy, Entropy, and Free Energy Changing at the selected temperatures.
- Also K (equilibrium constant) values are also available in the results.

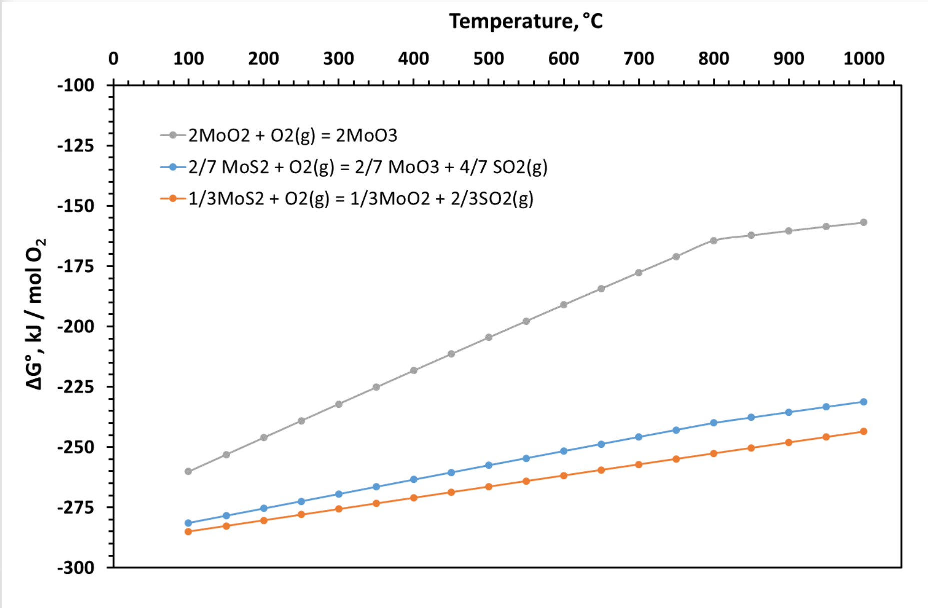
Source: HSC Chemistry

Material & Energy Balance



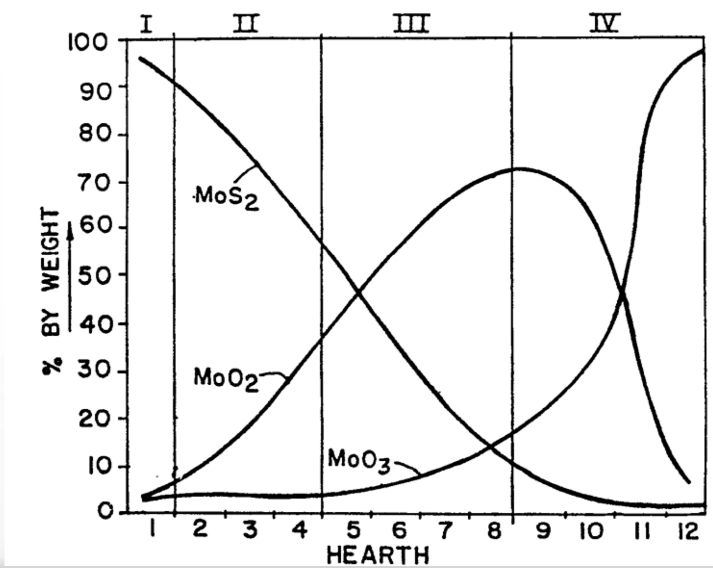
Source: HSC Chemistry

Material & Energy Balance



- The lowest energy obtaining reaction is the most favorable ones. So, MoO_2 formation reaction is firstly occurred. After consumption of all MoS_2 phase, MoO_3 formation reaction can be started.

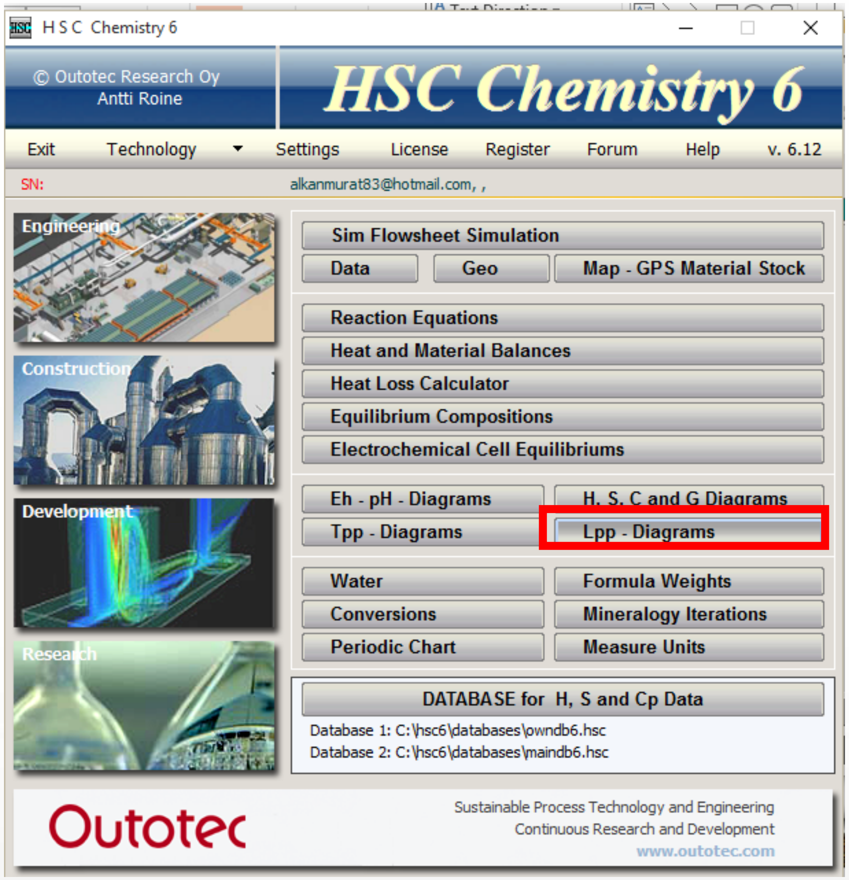
- Because of this reason, multiple hearth furnace (12-16 hearth) is commonly used for calcination of molybdenite concentration.



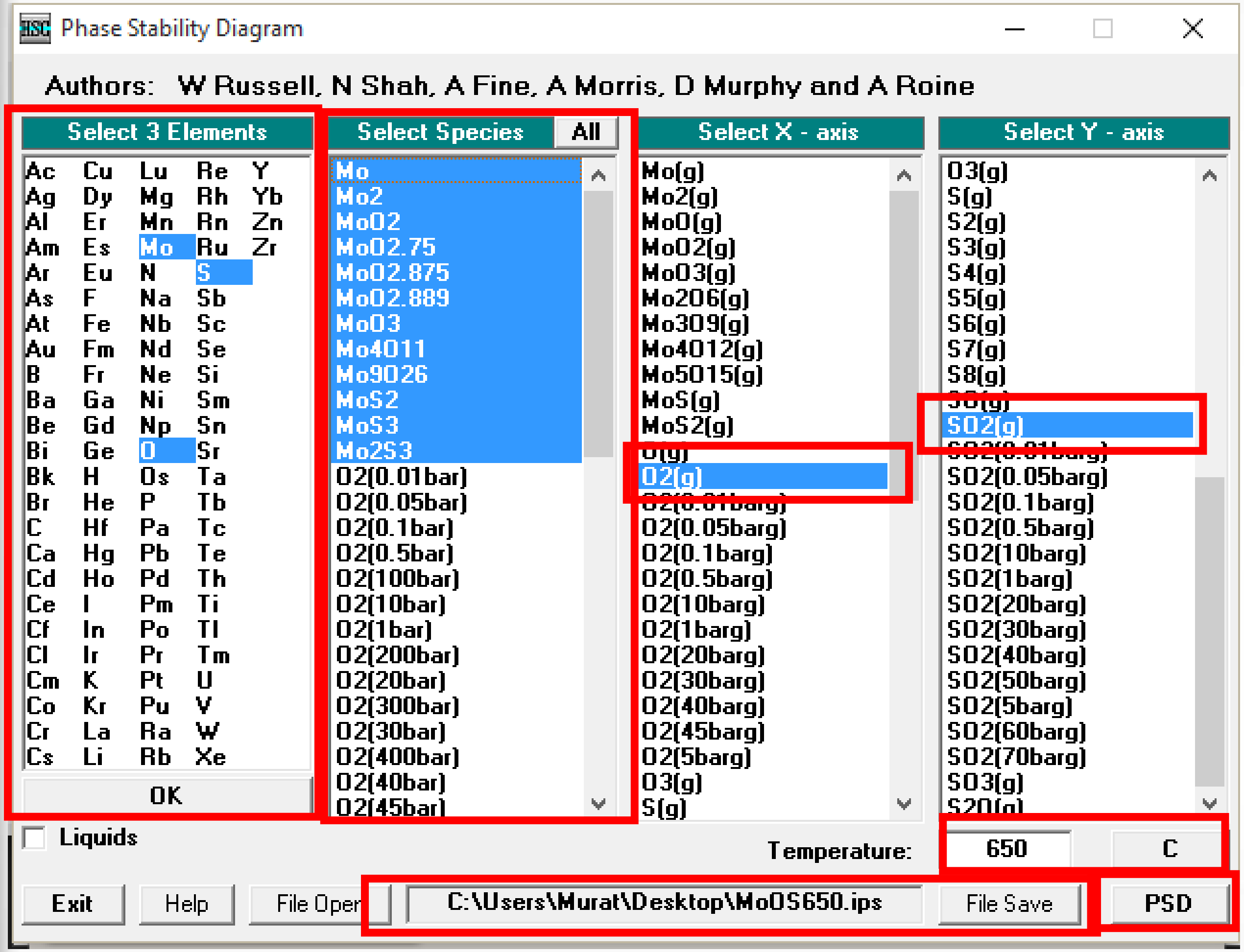
Source: HSC Chemistry

Material & Energy Balance

- In Sulphur containing systems, we can also use Kellogg Diagrams. To plot Kellogg Diagram (Mo-O-S Stability diagram) we can use "LPP-Diagrams" module in HSC.



Material & Energy Balance



1- Select the elements

(Mo, O, S)

then click OK

2- Select the species appeared in the diagram

3- Select the axises.

X-axis O_2 partial pressure

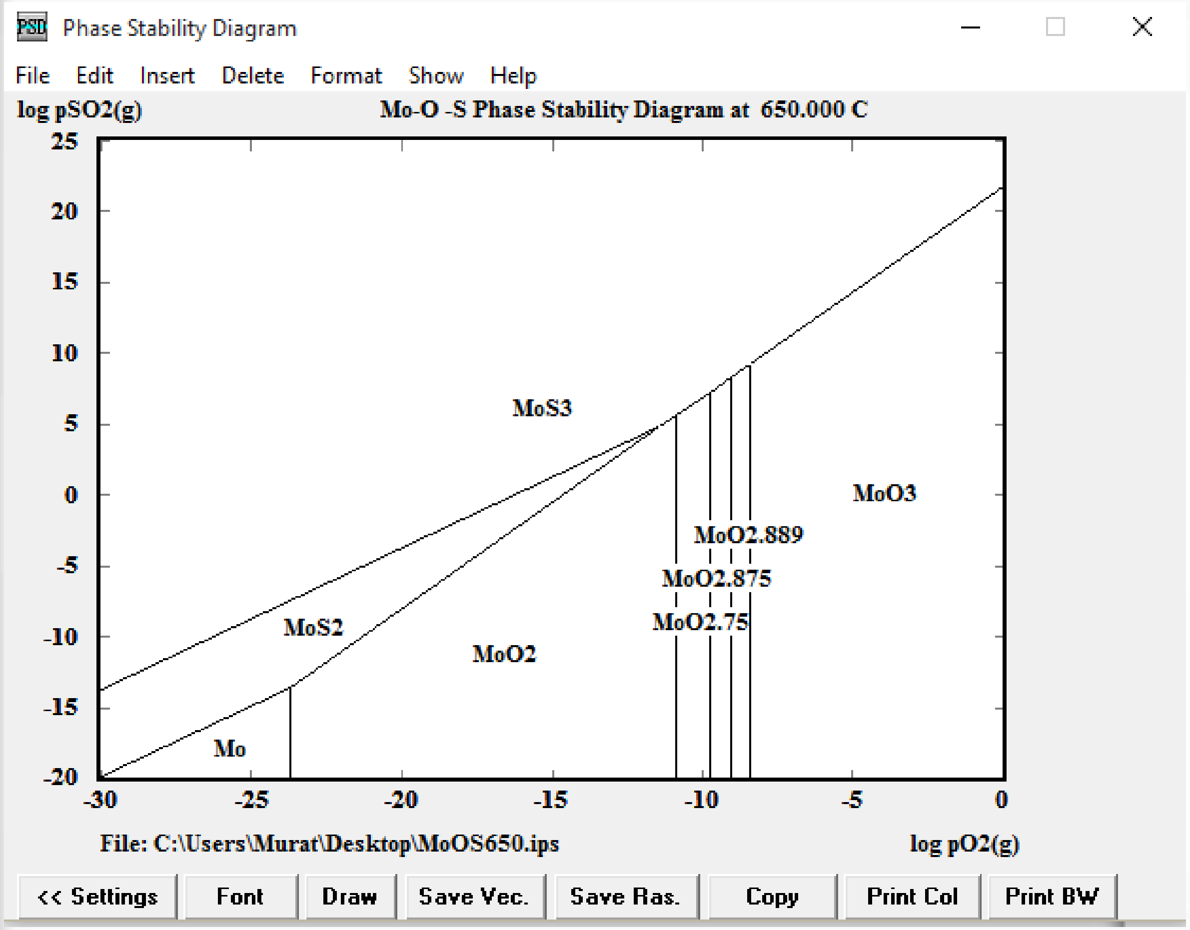
Y-axis SO_2 partial pressure

4- Select the temperature

5- Save file to a folder

6- Click PSD to plot diagram

Material & Energy Balance



- As we can see from the figure, MoO_2 will be formed firstly for producing MoO_3. $MoO_{2.75}$, $MoO_{2.875}$, $MoO_{2.889}$ phases can be occurred during the reaction.
- For final product formation we need to calculate partial pressure of gases.

Source: HSC Chemistry

Material Balance

- Let consider that we have 1 ton of concentrate with: 51.0 % Mo, 34.56 % S, 1.2 % Cu, 0.2 % Fe, 0.4 % Pb, 1.1 % SiO_2 by mass. Rest are water-moisture (11.34%) and oil (0.2 %).
- In concentrate, there are MoS_2, Cu_2S, FeS, PbS, SiO_2, H_2O, C compounds. Total:
- 850.9 kg MoS_2 = 5.316 kmol
- 15.0 kg Cu_2S = 0.094 kmol
- 3.1 kg FeS = 0.035 kmol
- 4.6 kg PbS = 0.019 kmol
- 12.0 kg SiO_2 = 0.200 kmol
- 113.4 kg H_2O = 6.300 kmol
- 2.0 kg Oil (C) = 0.166 kmol

Material Balance

- We have 1 ton of concentrate, reacted at 650 °C, with 99.5% reaction efficiency (for MoS_2). MoO_3 to MoO_2 conversion is 90 %.
- We use 25% excess air for calcinations. The reactions are:

$$2\ MoS_2 + 7\ O_{2(g)} = 2\ MoO_3 + 4\ SO_{2(g)}$$

$$MoS_2 + 3\ O_{2(g)} = MoO_2 + 2\ SO_{2(g)}$$

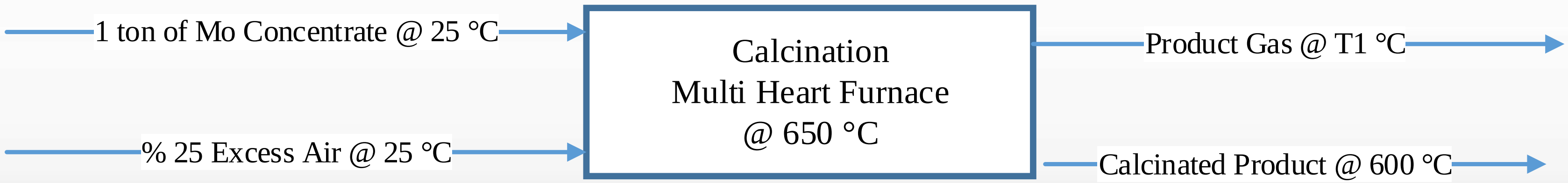
$$Cu_2S + 3/2\ O_{2(g)} = Cu_2O + SO_{2(g)}$$

$$FeS + 3/2\ O_{2(g)} = FeO + SO_{2(g)}$$

$$PbS + 3/2\ O_{2(g)} = PbO + SO_{2(g)}$$

$$H_2O_{(l)} = H_2O_{(g)}$$

$$C + O_{2(g)} = CO_{2(g)}$$



Source: ...

Material Balance

- For 99.5% reaction efficiency: 5.316 x 99.5% = 5.289 kmol MoS_2 will react. 5.316 – 5.289 = 0.027 kmol MoS_2 unreacted.
- For 90% MoO3 conversion: 5.289 x 90% = 4.760 kmol MoS_2 will react into MoO_3. 5.289 – 4.760 = 0.529 kmol MoS_2 will react into MoO_2.

$$2\ MoS_2 + 7\ O_{2(g)} = 2\ MoO_3 + 4\ SO_{2(g)}$$

4.760 kmol MoS_2 require 4.760 x 7 / 2 = 16.66 kmol O_2

4.760 kmol MoO_3 and 9.520 kmol SO_2 formed

$$MoS_2 + 3\ O_{2(g)} = MoO_2 + 2\ SO_{2(g)}$$

0.529 kmol MoS_2 require 0.529 x 3 = 1.587 kmol O_2

0.529 kmol MoO_2 and 1.058 kmol SO_2 formed

Source: …

Material Balance

$$Cu_2S + 3/2\ O_{2(g)} = Cu_2O + SO_{2(g)}$$

0.094 kmol Cu_2S + 0.141 kmol O_2 = 0.094 kmol Cu_2O + 0.094 kmol SO_2

$$FeS + 3/2\ O_{2(g)} = FeO + SO_{2(g)}$$

0.035 kmol FeS + 0.053 kmol O_2 = 0.035 kmol FeO + 0.035 kmol SO_2

$$PbS + 3/2\ O_{2(g)} = PbO + SO_{2(g)}$$

0.019 kmol PbS + 0.0,029 kmol O_2 = 0.019 kmol PbO + 0.019 kmol SO_2

$$H_2O_{(l)} = H_2O_{(g)}$$

6.300 kmol H_2O = 6.300 kmol H_2O

$$C + O_{2(g)} = CO_{2(g)}$$

0.166 kmol C + 0.166 kmol O_2 = 0.166 CO_2

Total O_2 require = 18.636 kmol (100% stoichiometric)

with 25% excess 18.636 + (18.636 x 25%) = 23.295 kmol O_2

Source: …

Material Balance

Total N_2 require = 23.295 x 0.79 / 0.21 = 87.634 kmol N_2

Total SO_2 produced = 10.726 kmol

Total input:

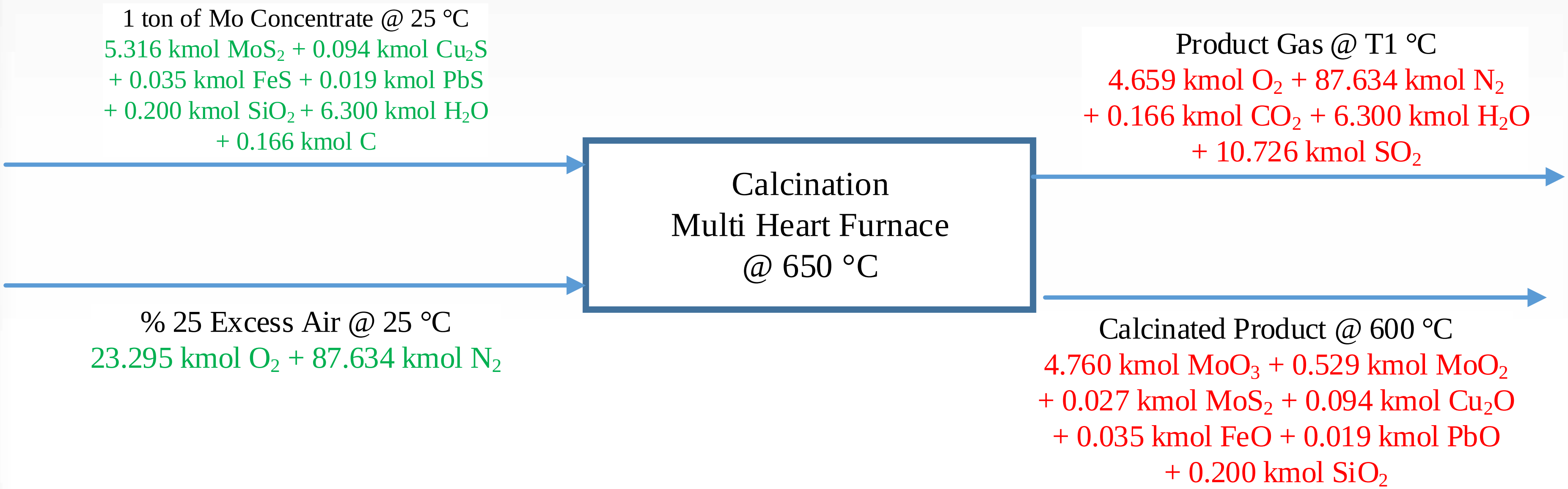
5.316 kmol MoS_2 + 0.094 kmol Cu_2S + 0.035 kmol FeS +
0.019 kmol PbS + 0.200 kmol SiO_2 + 6.300 kmol H_2O + 0.166 kmol C
+ 23.295 kmol O_2 + 87.634 kmol N_2

Total output:

4.760 kmol MoO_3 + 0.529 kmol MoO_2 + 0.027 kmol MoS_2
+ 0.094 kmol Cu_2O + 0.035 kmol FeO + 0.019 kmol PbO
+ 0.200 kmol SiO_2 + 4.659 kmol O_2 + 87.634 kmol N_2 + 0.166 kmol CO_2
+ 6.300 kmol H_2O + 10.726 kmol SO_2

Source: …

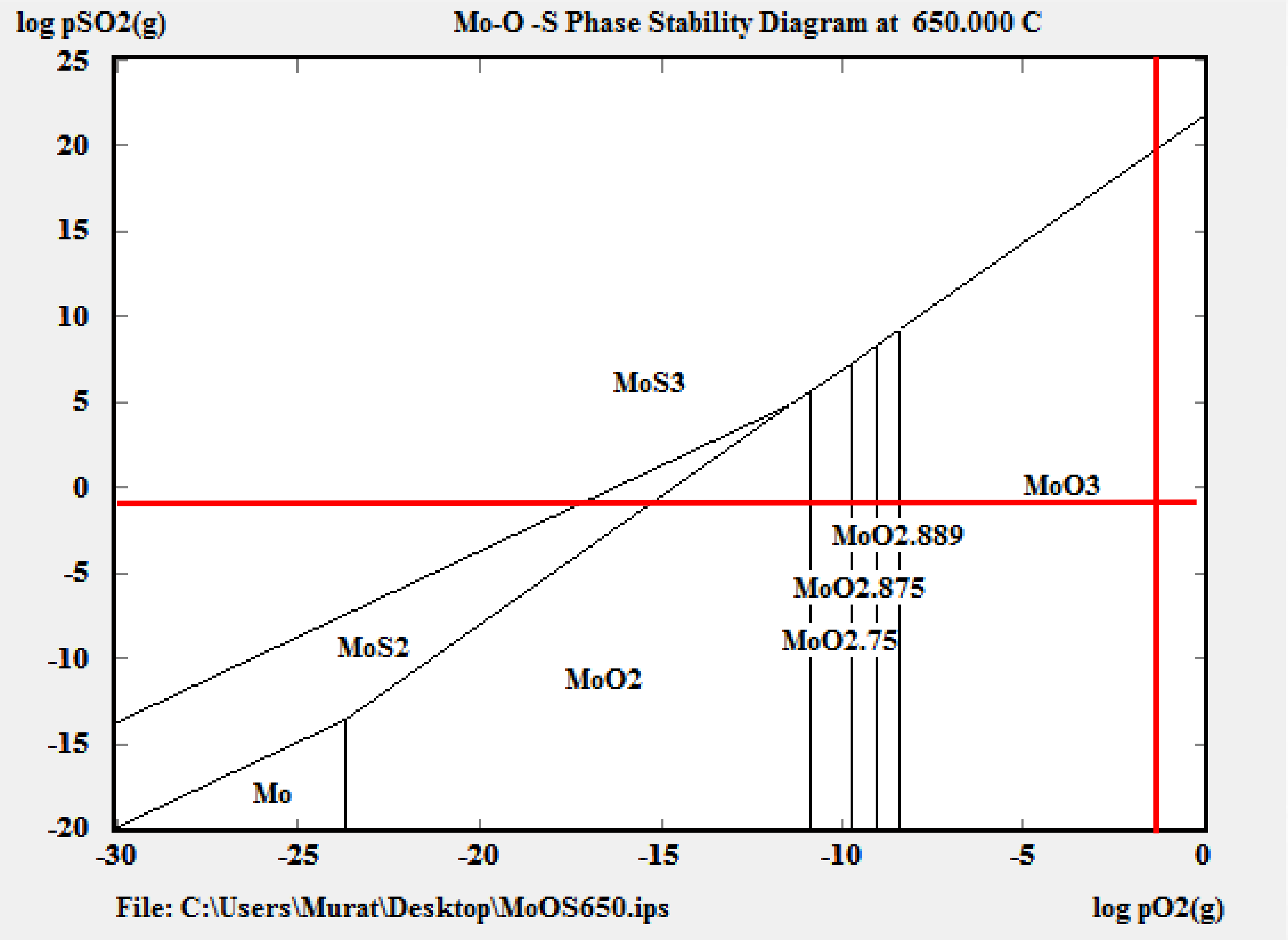
Material Balance



Product gas has 4.26 % O_2, 80.04 % N_2, 9.80 % SO_2, 5.75 % H_2O, 0.15 % CO_2

$\log p_{O_2} = -1.37 \quad \log p_{SO_2} = -1.01$

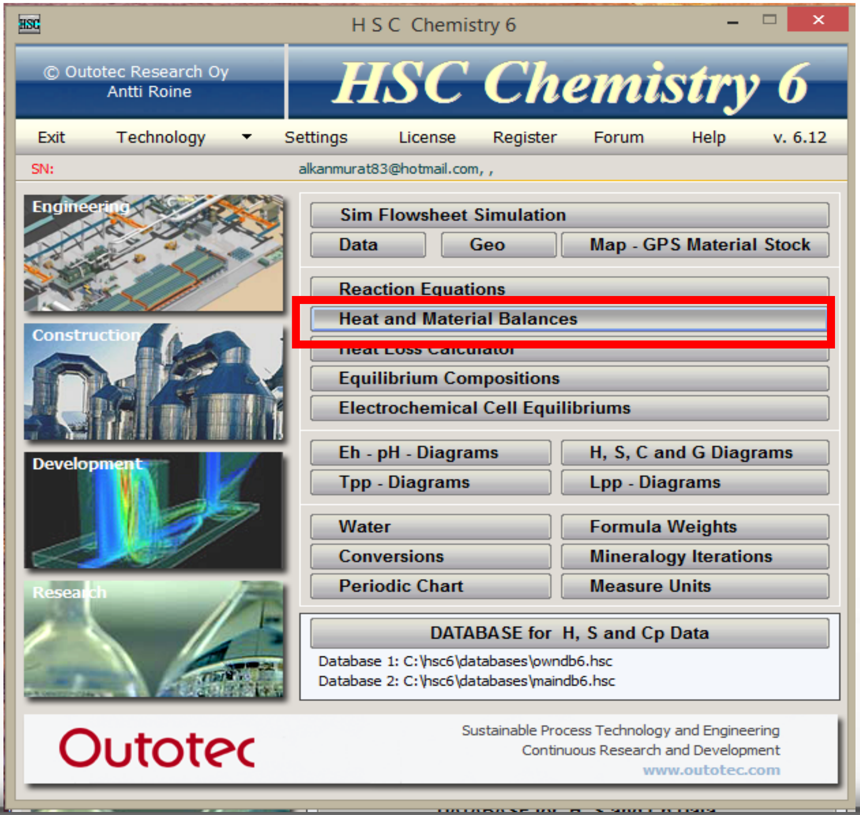
Source: ...



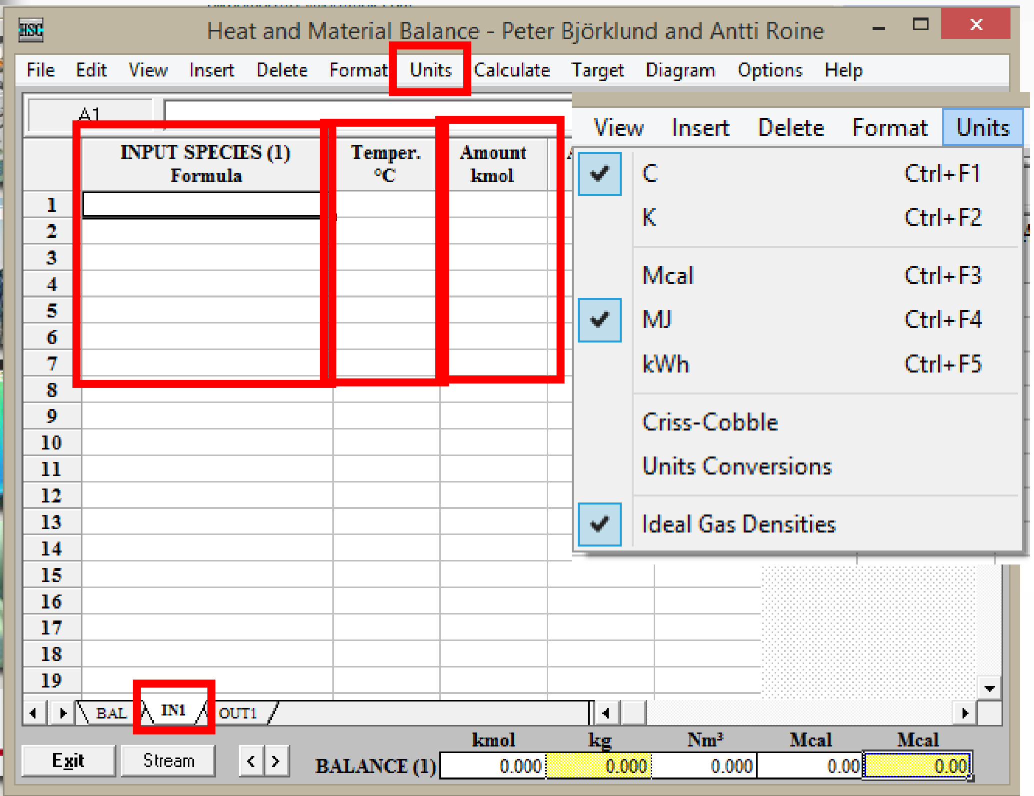
Source: HSC Chemistry

Energy Balance

- Our raw materials and air have entered the calcination furnace at 25 °C temperature. So Firstly, we use energy to heat up the raw materials at the reaction temperature (650 °C). For calculating energy requirement, we can use “Heat and Material Balance” module of HSC.



Energy Balance

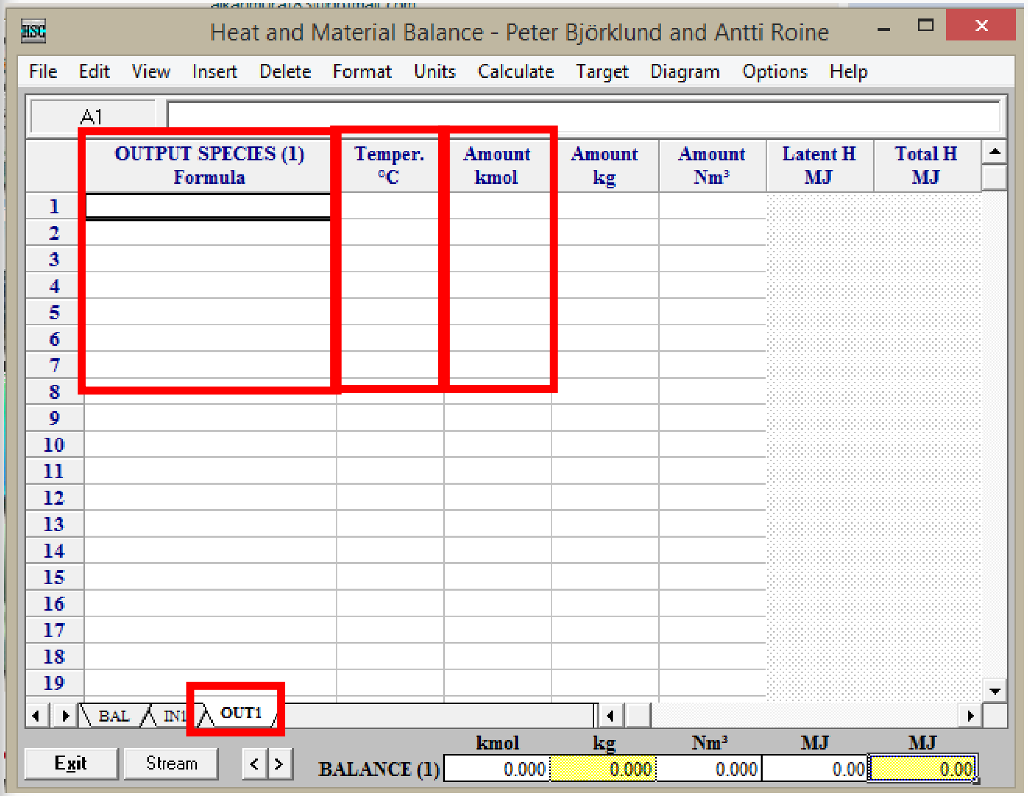


- In this module:

1- Firstly we choose our units by clicking Unit tab.

2- In 'In1' window, we can write the formula, amount and temperature of raw materials.

Energy Balance



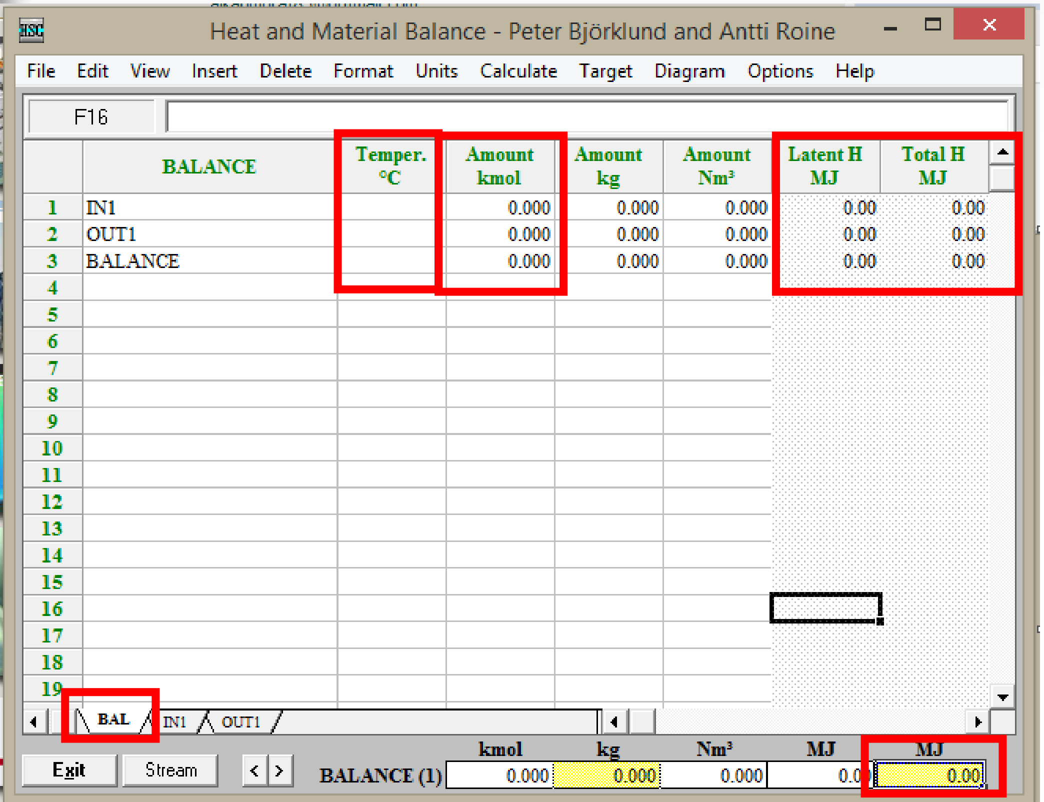
- In this module:

1- Firstly we choose our units by clicking Unit tab.

2- In 'In1' window, we can write the formula, amount and temperature of raw materials.

3- In 'Out1' window, we can write the formula, amount and temperature of products.

Energy Balance



- In this module:

1- Firstly we choose our units by clicking Unit tab.

2- In 'In1' window, we can write the formula, amount and temperature of raw materials.

3- In 'Out1' window, we can write the formula, amount and temperature of products.

4- In 'Bal' window, we can see amount, temperature and energy values of Input, Output and Balance states.

Energy Balance

Heat and Material Balance - Peter Björklund and Antti Roine

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

A12

	INPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	MoS2	25.000	5.316	850.879	0.168	0.00	-1467.98
2	Cu2S	25.000	0.094	14.960	0.003	0.00	-7.47
3	FeS	25.000	0.035	3.077	0.001	0.00	-3.56
4	PbS	25.000	0.019	4.546	0.001	0.00	-1.87
5	SiO2	25.000	0.200	12.017	0.005	0.00	-182.17
6	H2O	25.000	6.300	113.496	0.124	0.00	-1800.73
7	C	25.000	0.166	1.994	0.001	0.00	0.00
8	O2(g)	25.000	23.295	745.412	522.125	0.00	0.00
9	N2(g)	25.000	87.634	2454.926	1964.193	0.00	0.00
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							

BAL IN1 OUT1 In1-% Out1-%

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	0.000	0.000	141.082	2536.10	2813.32

Exit Stream

Our Input temperature is 25 °C

!!! Attention !!!

Do not forget to write (g) for all gaseous phases

- Let apply for our example.

Total input:

5.316 kmol MoS_2

0.094 kmol Cu_2S

0.035 kmol FeS

0.019 kmol PbS

0.200 kmol SiO_2

6.300 kmol H_2O

0.166 kmol C

23.295 kmol O_2

87.634 kmol N_2

Energy Balance

Heat and Material Balance - Peter Björklund and Antti Roine

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

E14

	OUTPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	MoS2	650.000	5.316	850.879	0.168	245.19	-1222.79
2	Cu2S	650.000	0.094	14.960	0.003	5.76	-1.72
3	FeS	650.000	0.035	3.077	0.001	1.50	-2.06
4	PbS	650.000	0.019	4.546	0.001	0.62	-1.24
5	SiO2	650.000	0.200	12.017	0.005	8.03	-174.15
6	H2O(g)	650.000	6.300	113.496	141.206	144.27	-1379.23
7	C	650.000	0.166	1.994	0.001	1.69	1.69
8	O2(g)	650.000	23.295	745.412	522.125	466.85	466.85
9	N2(g)	650.000	87.634	2454.926	1964.193	1662.21	1662.21
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							

BAL IN1 OUT1 In1-% Out1-%

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	0.000	0.000	0.000	2536.10	2536.10

Exit Stream

Our Input temperature is 650 °C

!!! Attention !!!

Do not forget to write (g) for all gaseous phases

- Let apply for our example.

Total input:

5.316 kmol MoS_2

0.094 kmol Cu_2S

0.035 kmol FeS

0.019 kmol PbS

0.200 kmol SiO_2

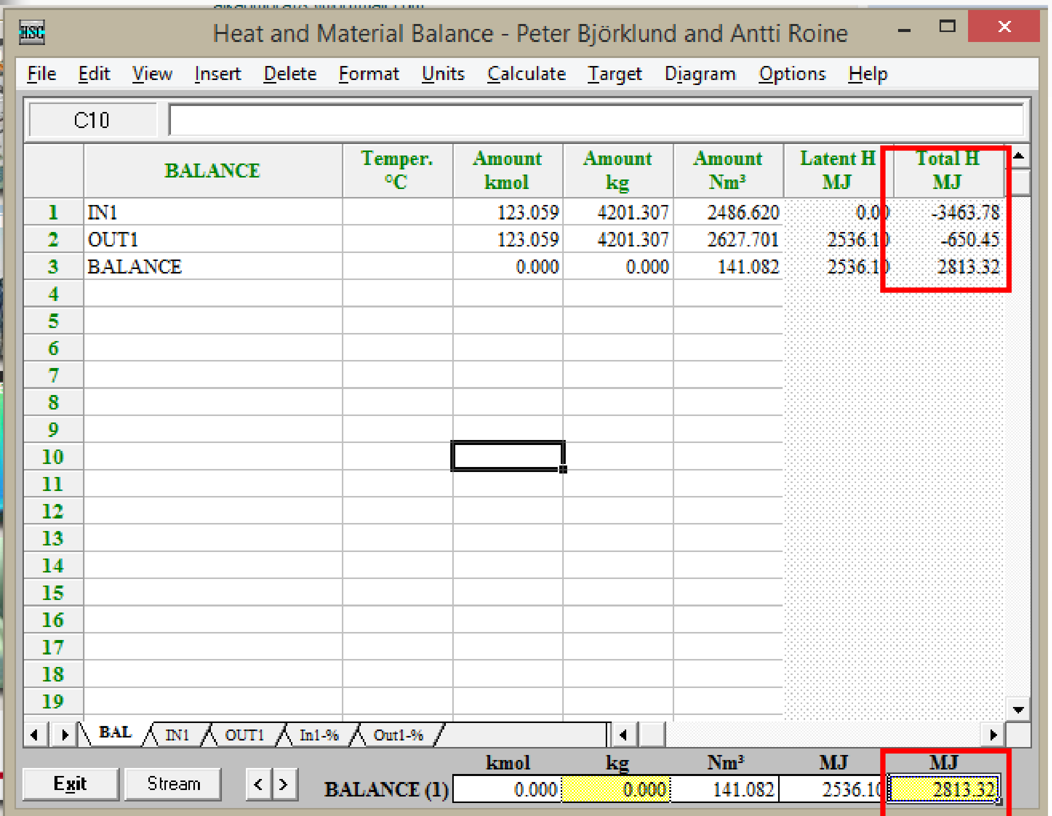
6.300 kmol H_2O

0.166 kmol C

23.295 kmol O_2

87.634 kmol N_2

Energy Balance



	BALANCE	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	IN1		123.059	4201.307	2486.620	0.00	-3463.78
2	OUT1		123.059	4201.307	2627.701	2536.10	-650.45
3	BALANCE		0.000	0.000	141.082	2536.10	2813.32

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	0.000	0.000	141.082	2536.1	2813.32

In Balance, we can see that we need 2813.32 MJ energy for 1 ton of concentrate to heat up from 25°C to 650°C

- Let apply for our example.

Total input:

5.316 kmol MoS_2

0.094 kmol Cu_2S

0.035 kmol FeS

0.019 kmol PbS

0.200 kmol SiO_2

6.300 kmol H_2O

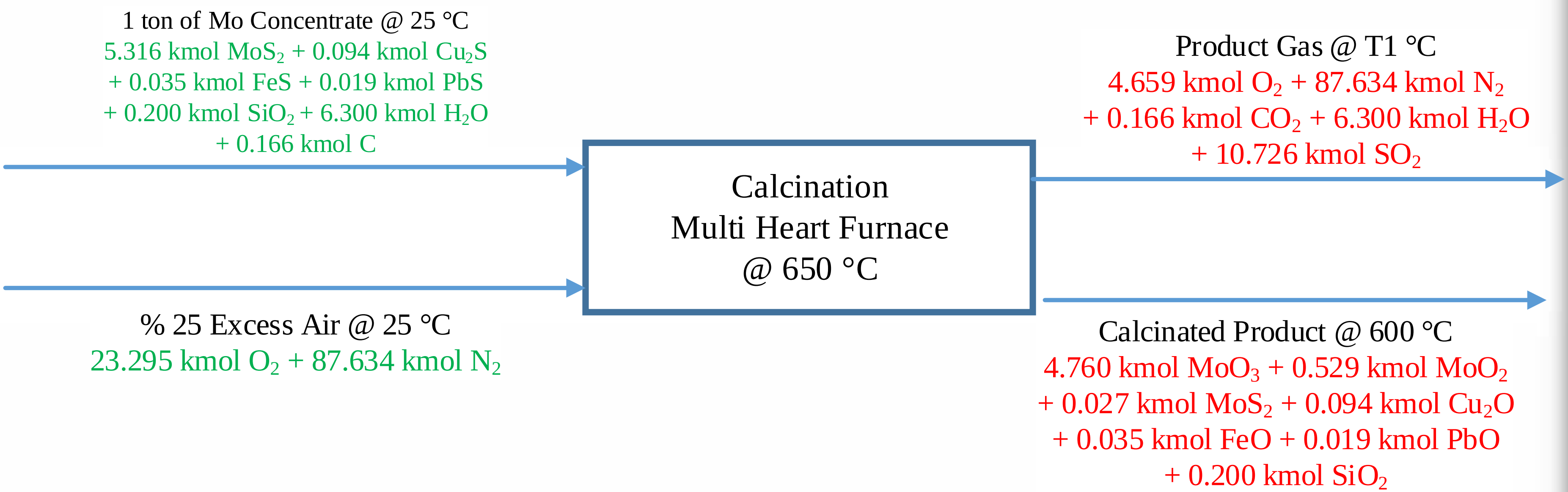
0.166 kmol C

23.295 kmol O_2

87.634 kmol N_2

Energy Balance for the Reaction

- Energy balance for the reaction



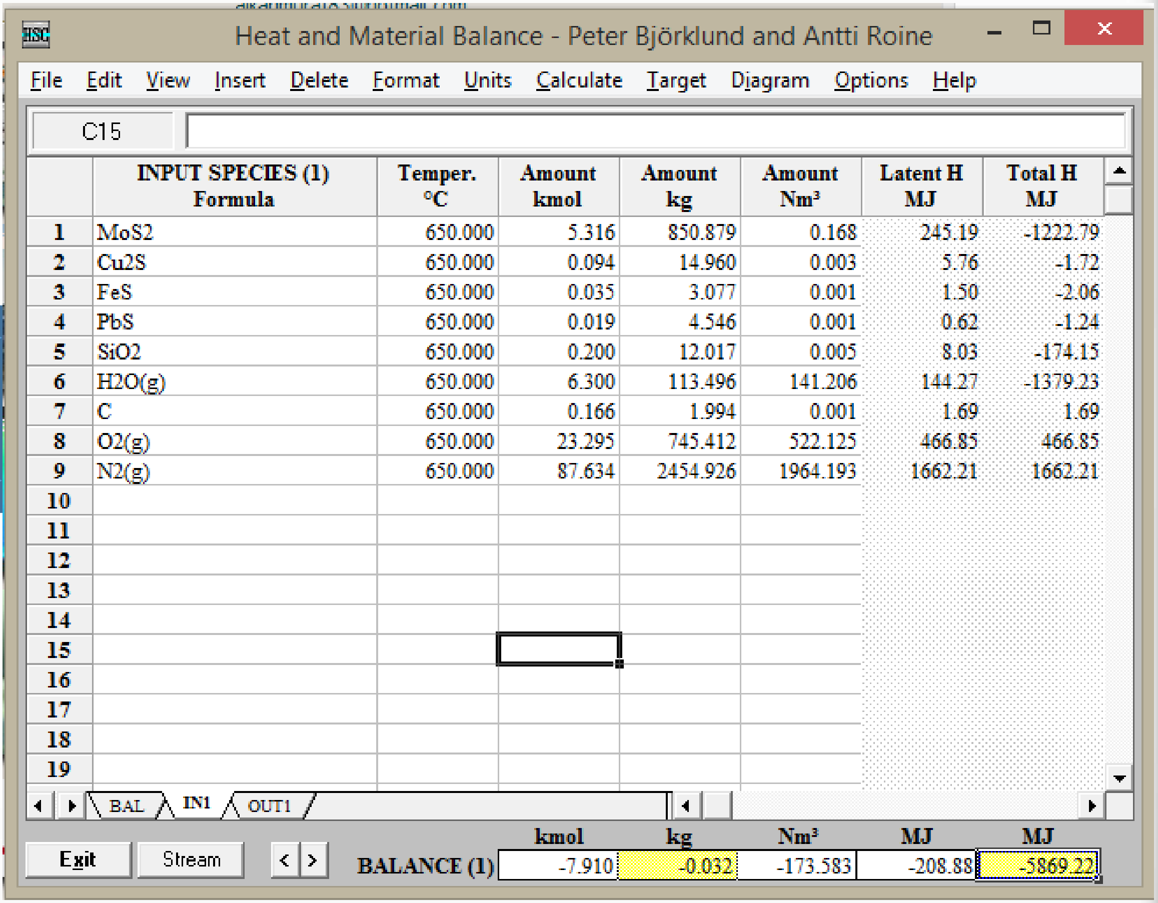
Source: …

Energy Balance for the Reaction

- Energy balance for the reaction

1 ton of Mo Concentrate @ 25 °C
5.316 kmol MoS_2 + 0.094 kmol Cu_2S + 0.035 kmol FeS + 0.019 kmol PbS + 0.200 kmol SiO_2 + 6.300 kmol H_2O + 0.166 kmol C

% 25 Excess Air @ 25 °C
23.295 kmol O_2 + 87.634 kmol N_2



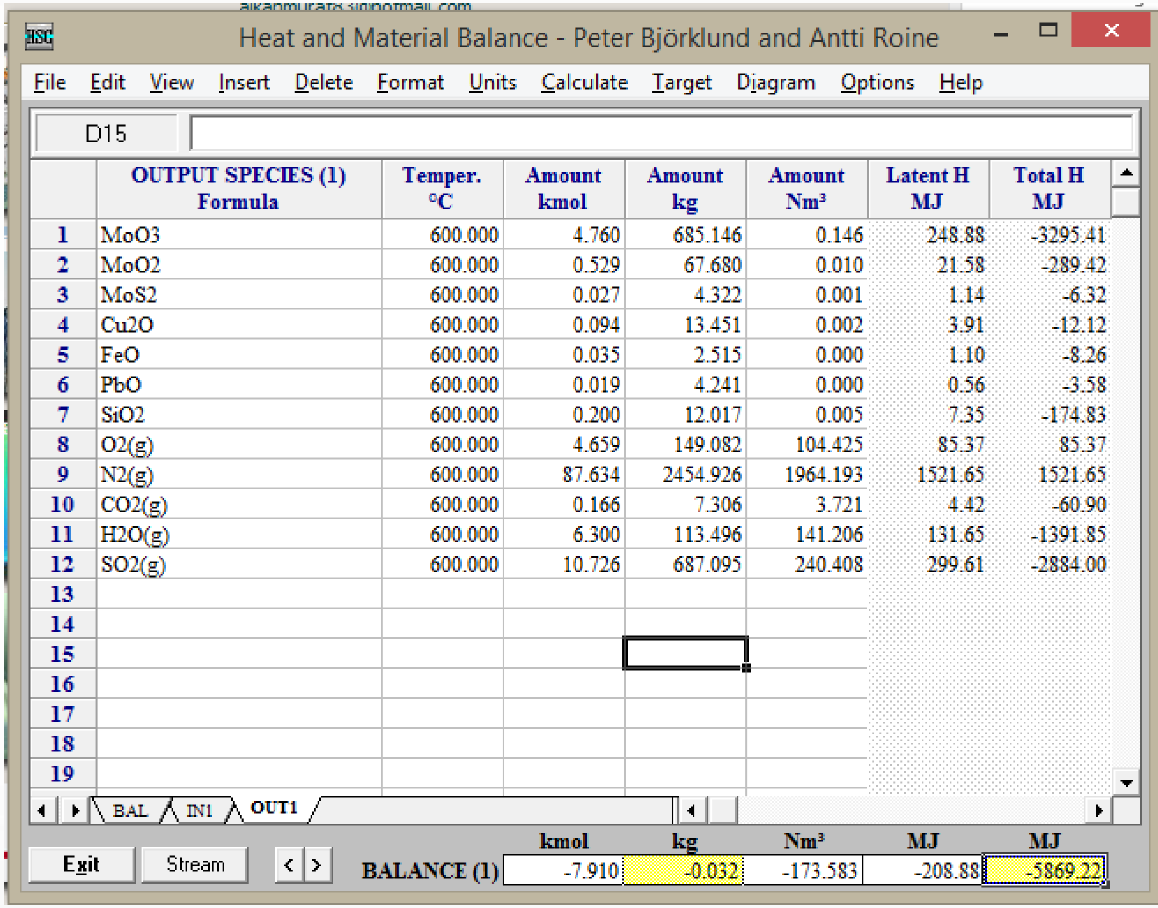
	INPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	MoS2	650.000	5.316	850.879	0.168	245.19	-1222.79
2	Cu2S	650.000	0.094	14.960	0.003	5.76	-1.72
3	FeS	650.000	0.035	3.077	0.001	1.50	-2.06
4	PbS	650.000	0.019	4.546	0.001	0.62	-1.24
5	SiO2	650.000	0.200	12.017	0.005	8.03	-174.15
6	H2O(g)	650.000	6.300	113.496	141.206	144.27	-1379.23
7	C	650.000	0.166	1.994	0.001	1.69	1.69
8	O2(g)	650.000	23.295	745.412	522.125	466.85	466.85
9	N2(g)	650.000	87.634	2454.926	1964.193	1662.21	1662.21
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-7.910	-0.032	-173.583	-208.88	-5869.22

Source: ...

Energy Balance for the Reaction

- Energy balance for the reaction



	OUTPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	MoO3	600.000	4.760	685.146	0.146	248.88	-3295.41
2	MoO2	600.000	0.529	67.680	0.010	21.58	-289.42
3	MoS2	600.000	0.027	4.322	0.001	1.14	-6.32
4	Cu2O	600.000	0.094	13.451	0.002	3.91	-12.12
5	FeO	600.000	0.035	2.515	0.000	1.10	-8.26
6	PbO	600.000	0.019	4.241	0.000	0.56	-3.58
7	SiO2	600.000	0.200	12.017	0.005	7.35	-174.83
8	O2(g)	600.000	4.659	149.082	104.425	85.37	85.37
9	N2(g)	600.000	87.634	2454.926	1964.193	1521.65	1521.65
10	CO2(g)	600.000	0.166	7.306	3.721	4.42	-60.90
11	H2O(g)	600.000	6.300	113.496	141.206	131.65	-1391.85
12	SO2(g)	600.000	10.726	687.095	240.408	299.61	-2884.00
13							
14							
15							
16							
17							
18							
19							

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-7.910	-0.032	-173.583	-208.88	-5869.22

Product Gas @ T1 °C

4.659 kmol O_2 + 87.634 kmol N_2 + 0.166 kmol CO_2 + 6.300 kmol H_2O + 10.726 kmol SO_2

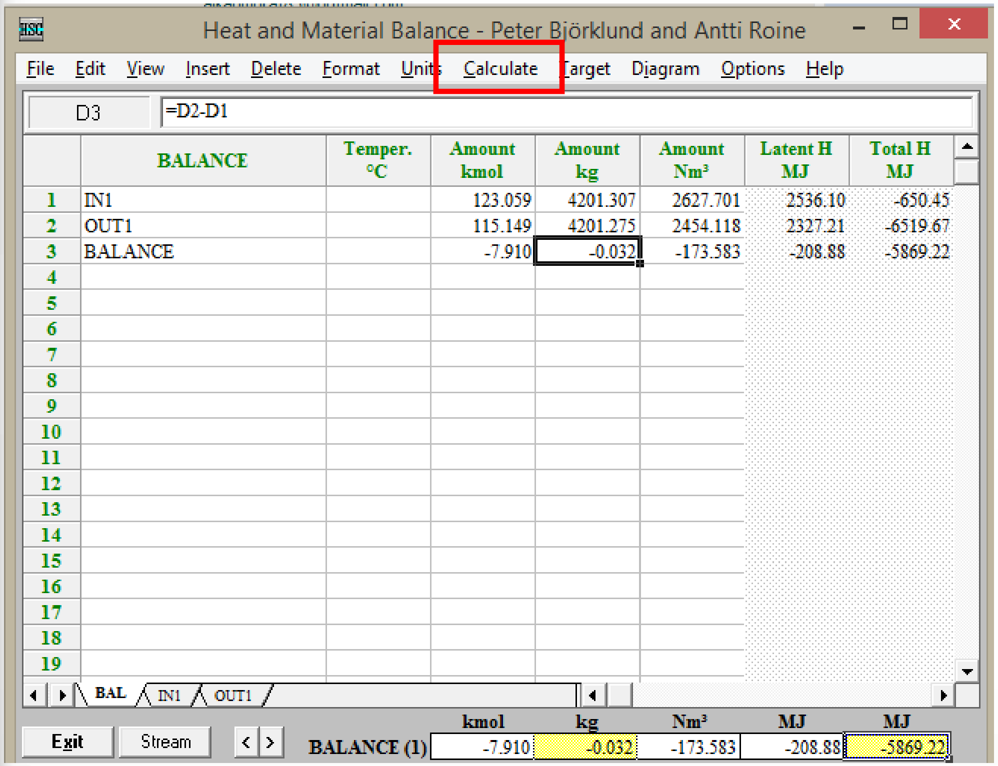
Calcinated Product @ 600 °C

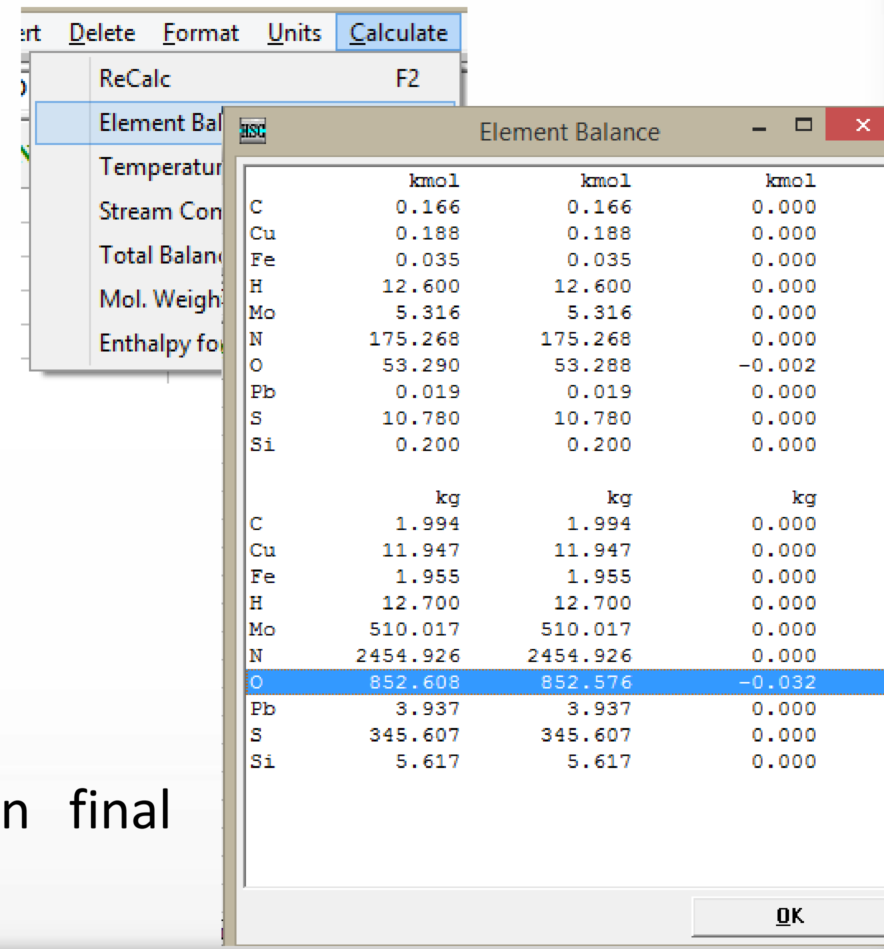
4.760 kmol MoO_3 + 0.529 kmol MoO_2 + 0.027 kmol MoS_2 + 0.094 kmol Cu_2O + 0.035 kmol FeO + 0.019 kmol PbO + 0.200 kmol SiO_2

Source: …

Energy Balance for the Reaction

- In balance we have 0.032 kg lost in products. To find the problem Click Calculate Tab and choose Element Balance



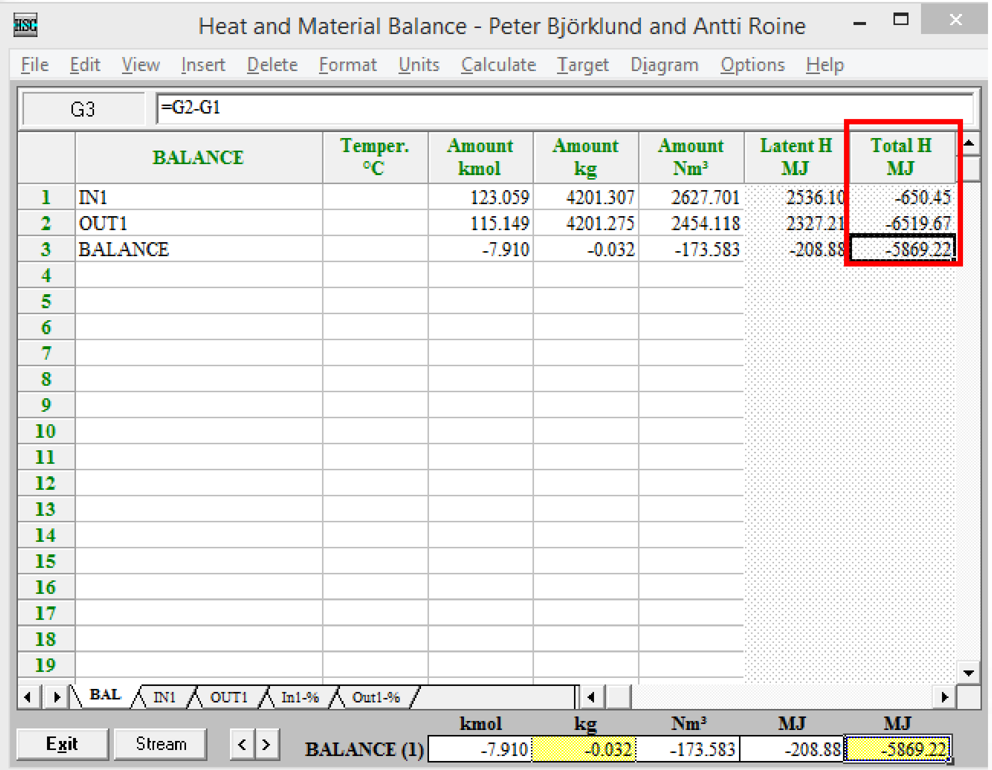


- There is 0.002 kmol O absence in final products. It can be negligible.

Source: …

Energy Balance for the Reaction

- In balance, 5869.22 MJ energy are generated during the reaction.
- This is an exothermic reaction



Heat and Material Balance - Peter Björklund and Antti Roine

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

G3 =G2-G1

	BALANCE	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	IN1		123.059	4201.307	2627.701	2536.10	-650.45
2	OUT1		115.149	4201.275	2454.118	2327.21	-6519.67
3	BALANCE		-7.910	-0.032	-173.583	-208.88	-5869.22

BAL IN1 OUT1 In1-% Out1-%

	kmol	kg	Nm³	MJ	MJ
BALANCE (1)	-7.910	-0.032	-173.583	-208.88	-5869.22

Exit Stream

- During the heating, we require 2813.32 MJ per ton Concentrate.
- And during the reaction we produce 5869.22 MJ per ton Concentrate.
- We can use these excess energy for heating the raw materials. And we have 3055.9 MJ per ton excess heat.

Source: ...

Energy Balance for the Reaction

- These 3055.9 MJ/t concentrate heat (energy) may be transferred by the off-gas. So, these excess heat will raise the off-gas outlet temperature from 600 °C to T °C.
- To find the maximum temperature of the off-gas in an **adiabatic** conditions; we will use

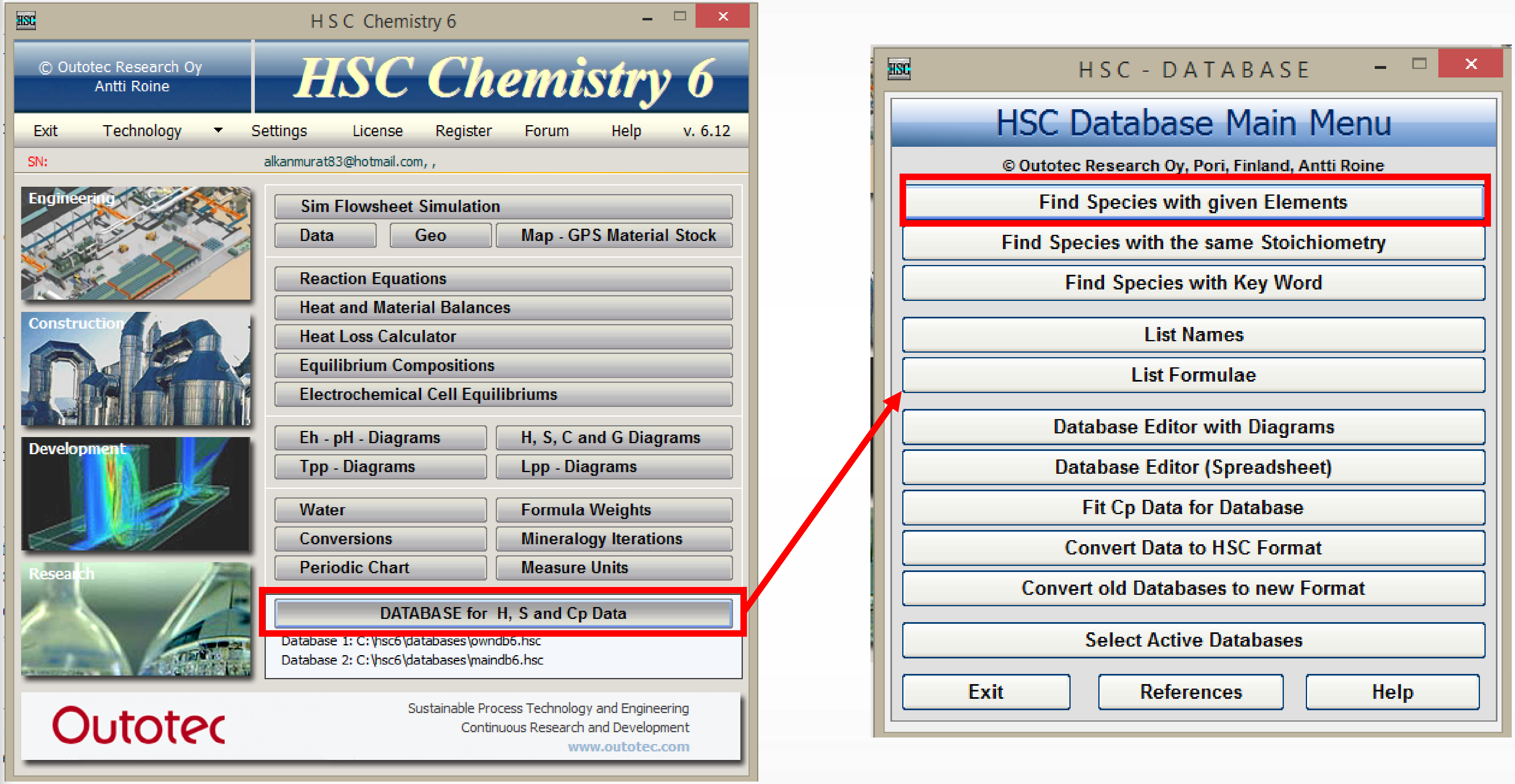
$$Q = \Delta H^{\circ}_{rxn} = H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p \times dT$$

- For finding Cp values we can use “Database” module of HSC.

$$C_{p,m} = a + b\,T + c\,T^2 + d\,T^3$$

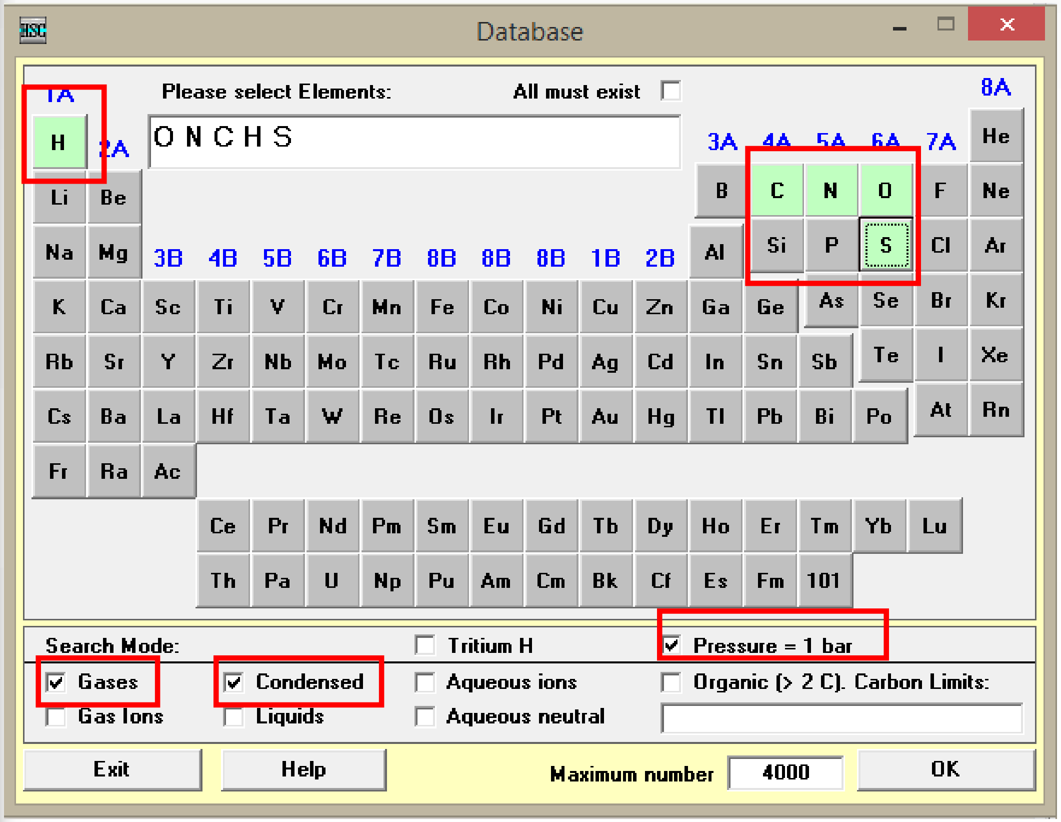
Source: …

Energy Balance for the Reaction



Source: …

Energy Balance for the Reaction

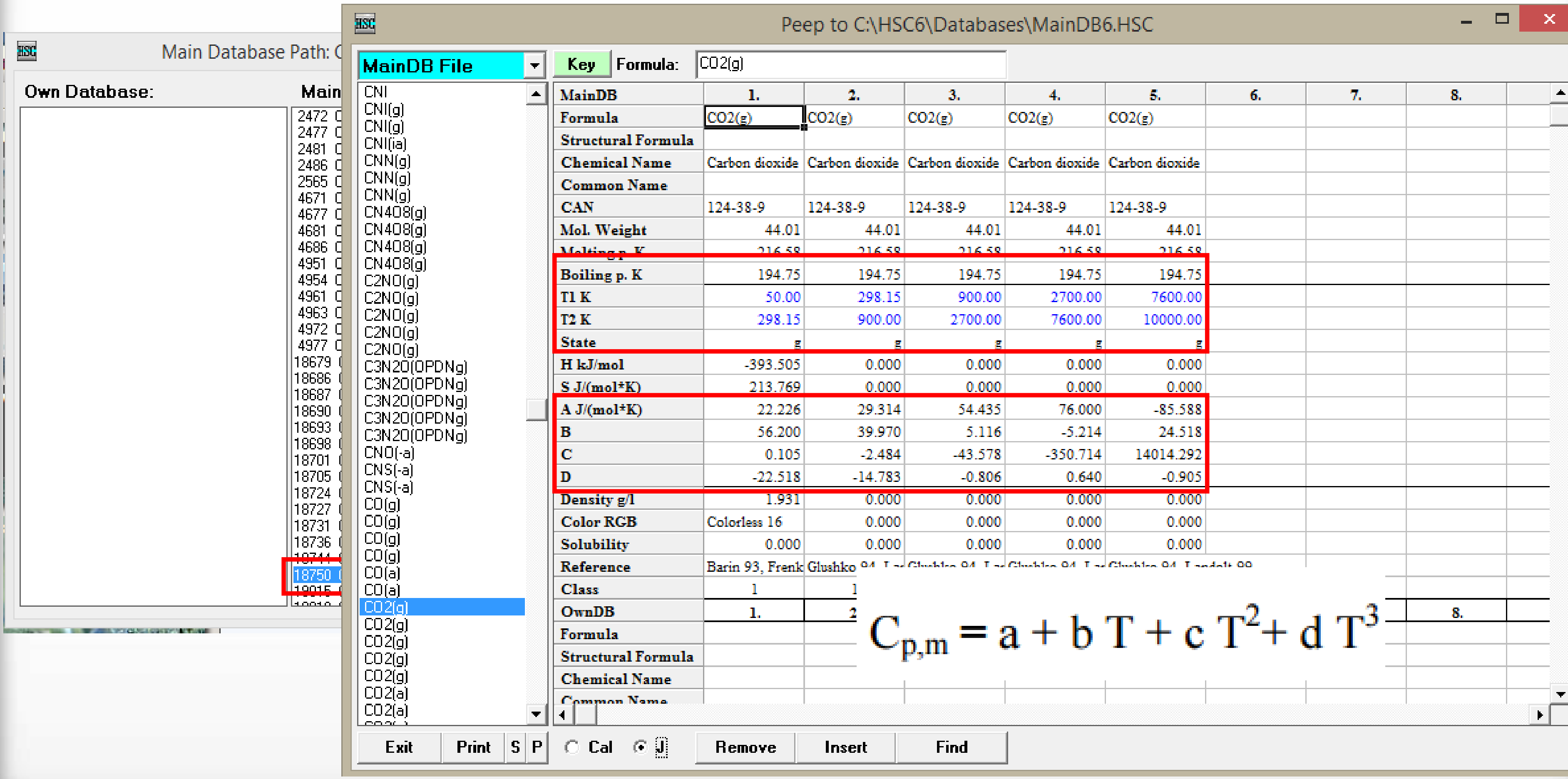


Then we click OK for the next step

- Firstly, we select the elements that considered.
- We are looking for gaseous and solid phases so, we select Gases and Condensed mode at 1 bar atmospheric pressure
- If we have Gas ions or liquids or aqueous ions, we also select these mode too.
- If we studied under pressure different than 1 bar we won’t select 1 bar pressure.

Energy Balance for the Reaction

- The program listed all the compounds available. If we click one of them we'll find its thermodynamical values.



MainDB	1.	2.	3.	4.	5.	6.	7.	8.
Formula	CO2(g)	CO2(g)	CO2(g)	CO2(g)	CO2(g)			
Structural Formula								
Chemical Name	Carbon dioxide	Carbon dioxide	Carbon dioxide	Carbon dioxide	Carbon dioxide			
Common Name								
CAN	124-38-9	124-38-9	124-38-9	124-38-9	124-38-9			
Mol. Weight	44.01	44.01	44.01	44.01	44.01			
Melting p. K	216.58	216.58	216.58	216.58	216.58			
Boiling p. K	194.75	194.75	194.75	194.75	194.75			
T1 K	50.00	298.15	900.00	2700.00	7600.00			
T2 K	298.15	900.00	2700.00	7600.00	10000.00			
State	g	g	g	g	g			
H kJ/mol	-393.505	0.000	0.000	0.000	0.000			
S J/(mol*K)	213.769	0.000	0.000	0.000	0.000			
A J/(mol*K)	22.226	29.314	54.435	76.000	-85.588			
B	56.200	39.970	5.116	-5.214	24.518			
C	0.105	-2.484	-43.578	-350.714	14014.292			
D	-22.518	-14.783	-0.806	0.640	-0.905			
Density g/l	1.931	0.000	0.000	0.000	0.000			
Color RGB	Colorless 16	0.000	0.000	0.000	0.000			
Solubility	0.000	0.000	0.000	0.000	0.000			
Reference	Barin 93, Frenk	Glushko 94, L...	Glushko 94, L...	Glushko 94, L...	Glushko 94, Landolt 99			
Class	1	1						

$$C_{p,m} = a + b\,T + c\,T^2 + d\,T^3$$

Source: …

Energy Balance for the Reaction

- Or we can easily use HSC Heat and Material Module

Heat and Material Balance - Peter Björklund and Antti Roine

File Edit View Insert Delete Format Units Calculate Target Diagram Options Help

	INPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	O2(g)	600.000	4.659	149.082	104.425	85.37	85.37
2	N2(g)	600.000	87.634	2454.926	1964.193	1521.65	1521.65
3	CO2(g)	600.000	0.166	7.306	3.721	4.42	-60.90
4	H2O(g)	600.000	6.300	113.496	141.206	131.65	-1391.85
5	SO2(g)	600.000	10.726	687.095	240.408	299.6	-2884.00
6							3055.90

Calculate: ReCalc F2; Element Balance F3; Temperature Balance F4; Stream Compositions F5; Total Balance; Mol. Weight; Enthalpy for Species

Heat and Material Balance - Peter Björklund and Antti Roine

	OUTPUT SPECIES (1) Formula	Temper. °C	Amount kmol	Amount kg	Amount Nm³	Latent H MJ	Total H MJ
1	O2(g)	600.000	4.659	149.082	104.425	85.37	85.37
2	N2(g)	600.000	87.634	2454.926	1964.193	1521.65	1521.65
3	CO2(g)	600.000	0.166	7.306	3.721	4.42	-60.90
4	H2O(g)	600.000	6.300	113.496	141.206	131.65	-1391.85
5	SO2(g)	600.000	10.726	687.095	240.408	299.61	-2884.00

Totals: Nm³ 0.000; MJ 0.00; MJ -3055.90

Temperature Balance

Temperature of products = 1358.3 C (when Heat Balance = 0)

OK

Source: ...