Expertise in wet chemical analysis – a route to success or totally obsolete?

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Overwiew

- What is pretreatment?
- Different sample types
- What is this?
  - Example 1 and 2
- Conclusion

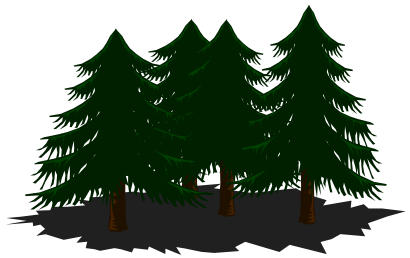
Pretreatment - Wet Chemistry

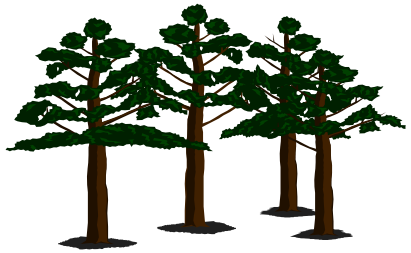
- Acidification
- Dilution
- Dry-Ashing (575ºC and/or 900ºC)
- Wet Digestion with nitric acid (HNO_3) in closed vessel
  - Microwave
- Fusion reactions
  - Acidic flux ($K_2S_2O_7$)
  - Basic flux ($KNaCO_3$)

Wet Digestion - Select reagents

- Sample type and Issue

- HNO_3 oxidizing organic material (CO_2, H_2O, NO_x)
- HNO_3 + H_2O_2 NO_x
- H_2O_2 + HNO_3 (SO_4)
- Aqua regia
- Aqua regia + HF
- HF
- H_2SO_4





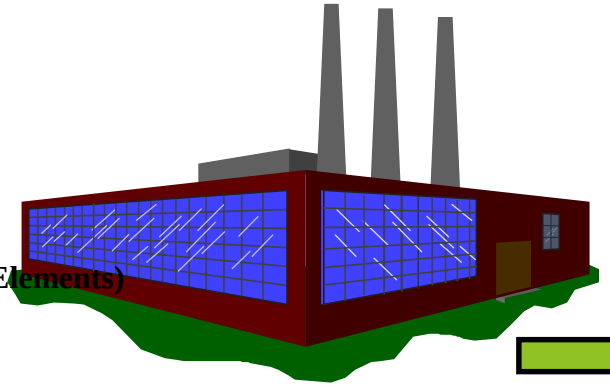
Pb Hg P Si Na K

Cd Cr As Ca Mg Mn

Al Cl

NPE

(Non Process Elements)

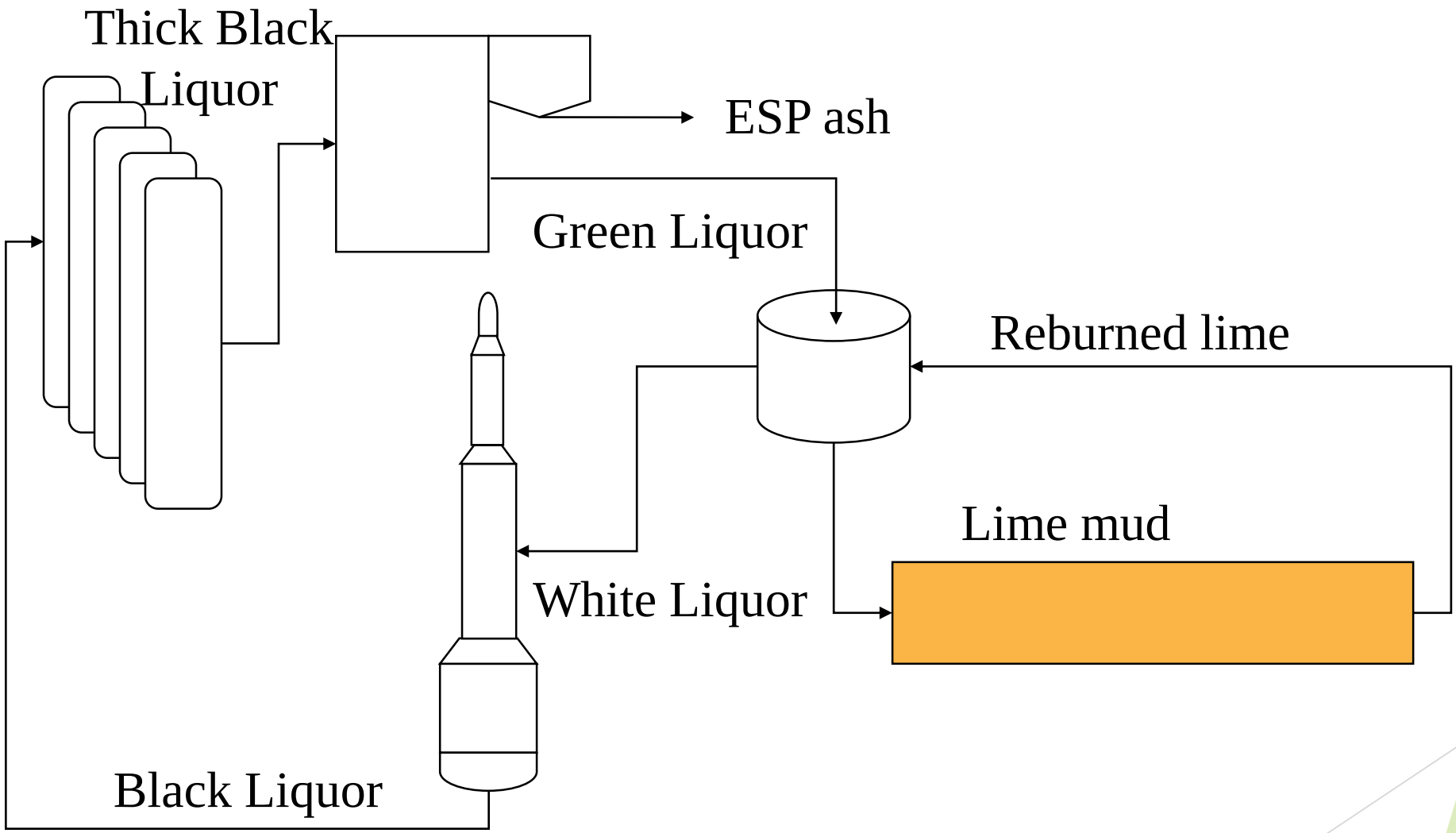


NPE

(Non Process Elements)

Pulp
Lime mud
Green Liquor sludge
Effluent
Grits

Recovery Area



Sample types - Pretreatment and End determination, past and present

Sample type	Pretreatment		End determination	
	förr	nu	förr	nu
Wood, Pulp, Board, Paper	Dry ashing-HCl or Open vessel-$HClO_4$	Mw-digestion HNO_3+**H_2O_2**	AAS-flame or AAS-THGA	ICP-OES ICP-MS
Black Liquor, 10%-75% DS	H_2O_2+HCl+ dry ashing	Mw-digestion **H_2O_2**+HNO_3	AAS-flame	
White Liquor, Green Liquor	H_2O_2+HCl			
ESP	HCl	Mw-digestion HNO_3		
Lime mud, Lime	HCl+ashing+HF			

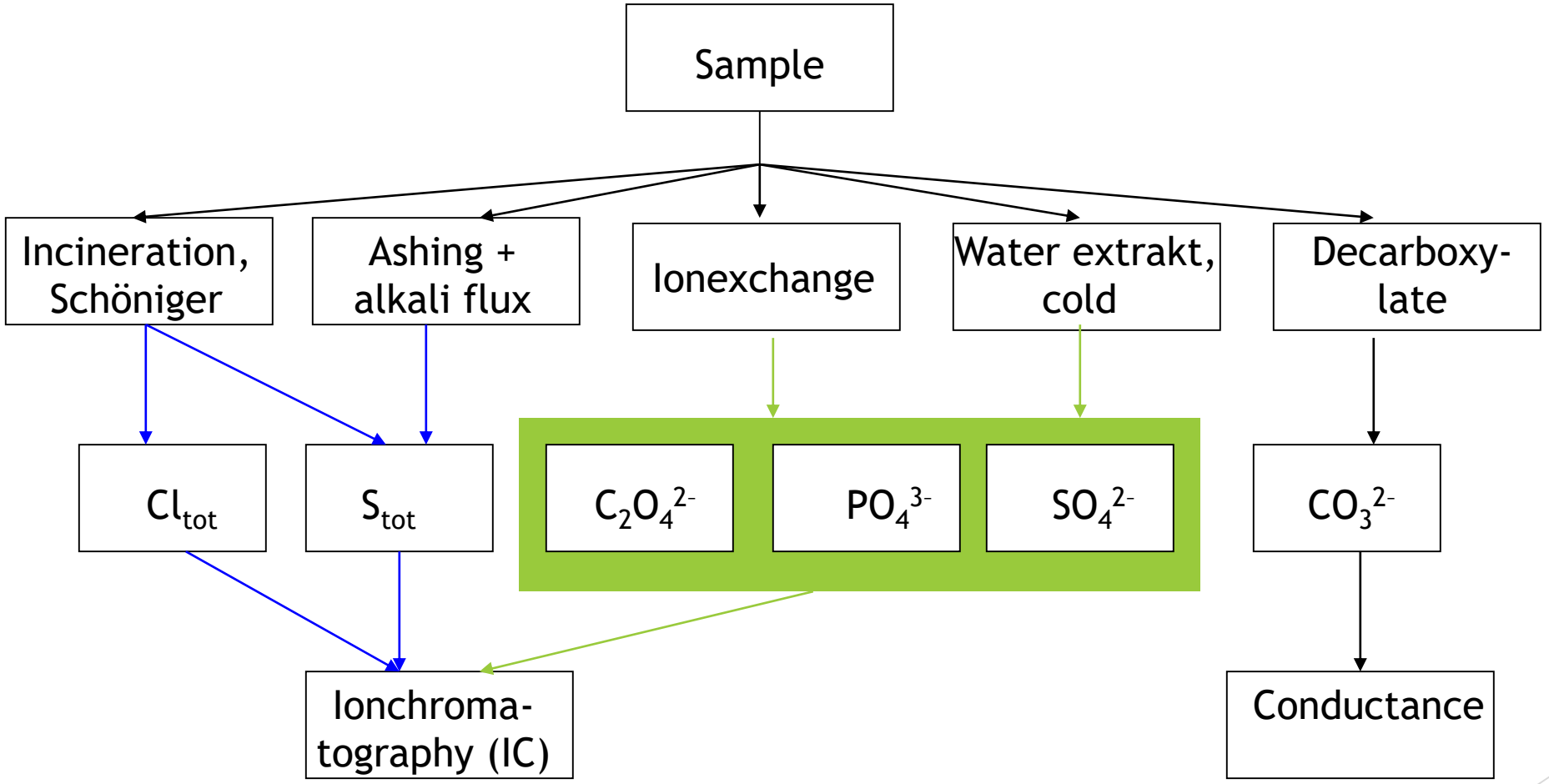
Sample – What is this?

The size of this ”stone piece” ~ 3 x 7 cm

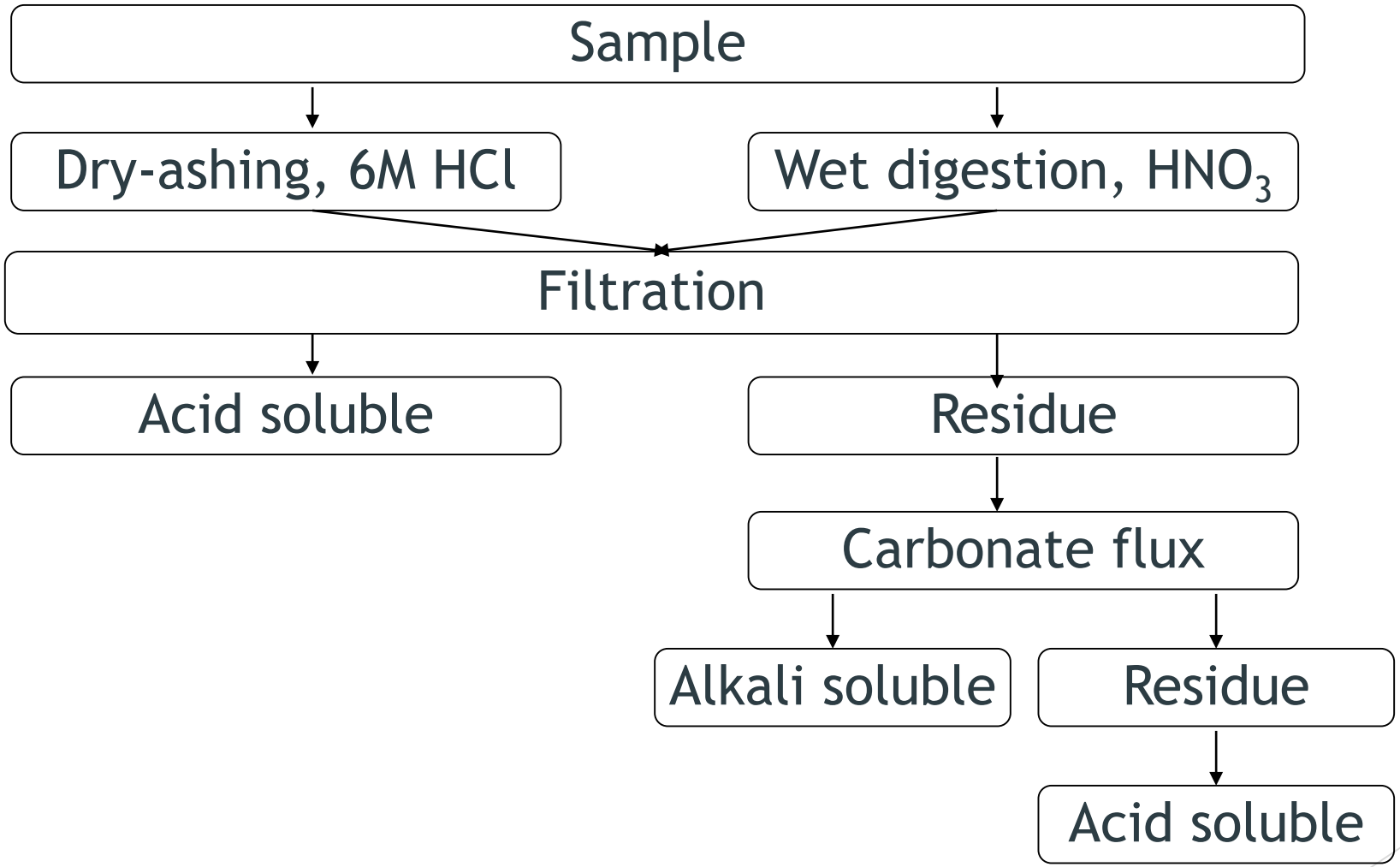
Analytical procedure - *Deposits*

- Origin
- Shape
- Texture
- Colour
- Smell
- Solubility
- Ash content
- Anion analysis
- Metal analysis
- Organic analysis

Anion analysis - *Deposits*



Metal analysis - *Deposits*



Deposit from Pulp mill no 1
Methods

- The ash content at 575°C, 3h and 900°C, 1h was determined.
- The anions were determined by ionchromatography, IC, after ion-exchange pre-treatment.
- The carbonate content was determined according to SCAN-N 32:88.
- The metal content was determined with ICP after dry-ashing and dissolution in HCl.
- The lignin was precipitated by the addition of HCl and determined gravimetrically.

Deposit from Pulp mill no 1
Analytical results

Analysis	Results (%w/w DS)
Ash content, 575°C	89
Ash content, 900°C	80
pH	10,6
Carbonate, CO_3^{2-}	15,6
Oxalate, $C_2O_4^{2-}$	<0,5
Sulphate, SO_4^{2-}	30,7
Sodium, Na	33,9
Potassium, K	2,7
Calcium, Ca	0,2
Iron, Fe	0,4
Lignin	13,9

What does these results mean

Ash content (575°C) = 89%
Ash content (900°C) = 80%
9% as CO_2 (12% CO_3) or others
Ca = 0,2 %

→

No $CaCO_3$ in this sample

CO_3 (analysed) = 15,6%
Na (analysed) = 33,9%

→

Na_2CO_3 = 26%

$M(CaCO_3)$ = 100 g/mol
M(CaO) = 56 g/mol
M(Ca) = 40 g/mol
$M(CO_2)$ = 44 g/mol
$M(CO_3)$ = 60 g/mol

$M(Na_2CO_3)$ = 106 g/mol
M(Na) = 23 g/mol

Deposit from a Pulp mill no 1 *Summary*

- The deposit consists mainly of Na_2SO_4, 45 %,Na_2CO_3, 26 % and NaOH, 15 %.
- The organic part of the deposit consists mainly of lignin, 14 %.
- The composition indicates that the origin of the deposit is oxidized black liquor.
- The deposit is totally water soluble
- The massratio between Na_2SO_4/Na_2CO_3 shows that the main part of the deposit consists of **burkeite**, 2 $Na_2SO_4.Na_2CO_3$.

Deposit from Pulp mill no 2
Methods

- The ash content at 575°C, 3h and 900°C, 1h was determined.
- The anions were determined by ionchromatography, IC, after ion-exchange pre-treatment.
- The carbonate content was determined according to SCAN-N 32:88.
- The metal content was determined with ICP after dry-ashing and dissolution in HCl.
- The lignin was precipitated by the addition of HCl and determined gravimetrically.

Deposit from Pulp mill no 2
Analytical results

Analysis	Results (%w/w DS)
Ash, 575°C	57
Ash, 900°C	48
pH	10,0
Carbonate, CO_3^{2-}	10,0
Oxalate, $C_2O_4^{2-}$	1,1
Sulphate, SO_4^{2-}	2,9
Sodium, Na	16
Potassium, K	3,2
Calcium, Ca	3,7
Magnesium, Mg	0,03
Lignin	17

Deposit from Pulp mill no 2
Summary

- The deposit consists mainly of sodium compounds, such as Na_2CO_3, 8 %, Na_2SO_4, 2 % and $Na_2C_2O_4$, 2 %.
  Some of the sodium can also be bounded to organic substances like lignin.
- There are also some $CaCO_3$, 8 % and $CaSO_4$, 2%.
- The organic part of the deposit consists mainly of lignin, 17 %.
- There is no or little burkeite, 2 $Na_2SO_4.Na_2CO_3$,in the deposit.
- The deposit is almost totally water soluble.

Conclusion

Expertise in wet chemical analysis –
a route to success or totally obsolete???