Elements and Industry:
The Chemical Revolution in the White Lead Industry (And the Cold Shower of Practice)

Ernst Homburg

23 May 2013

Department of History, Maastricht

Modern notion of element

- (a) Distinct kinds of atoms (specific number of protons)
- (b) Specific atomic weight (but: isotopes)
- (c) Atoms not destructable by chemical means

With hindsight this notion mainly goes back to:

- Lavoisier (1789): ‘elements’ are the ultimate remaining bodies of analytical decomposition;
- Dalton (1800): atomic theory: symbols for chemical elements

Gradual evolution for over more than a century

Early 17th century

- Aristotle's elements: earth, water, air, fire
- Paracelcus' principles: mercury, sulfur, salt

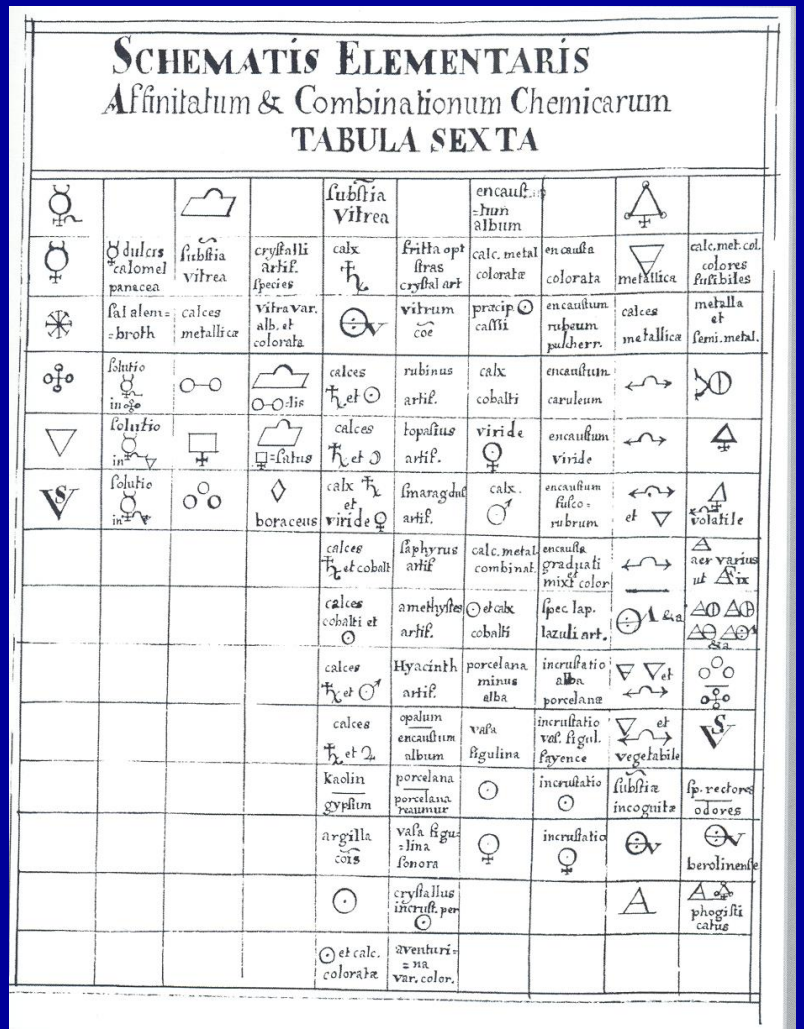
Ca. 1700

- Joachim Becher and Georg Ernst Stahl: phlogiston theory, combining in a way the elements and principles

18th century

- Increased understanding of double decomposition: AB + CD => AC + BD [Ba(OH)2 + K2SO4 => BaSO4 + 2KOH]

Etienne Geoffroy's affinity table (1718) summarized reactivity



SCHEMATIS ELEMENTARIS
Affinitatum & Combinationum Chemicarum
TABULA SEXTA

				Substia Vitrea		encaust.-tum album			
	☿ dulcis ☿ calomel panacea	Substia vitrea	crystalli artif. species	calx ♄	fritta opt stras crystal art	calc. metal coloratæ	encausta colorata	metallica	calc. met. col. colores fusibiles
	sal alem.= =broth	calces metallicæ	Vitra var. alb. et colorata	÷▽	vitrum ♀ coe	præcip. ☉ cassii	encaustum rubeum pulcherr.	calces metallicæ	metalla et semi. metal.
	solutio ☿ in ☌	○–○	○–○-dis	calces ♄ et ☉	rubinus artif.	calx cobalti	encaustum caruleum		
▽	solutio ☿ in ♄ ▽	□	□=fulus	calces ♄ et ☽	topasius artif.	viride ♀	encaustum viride		
▽	solutio ☿ in ♀	○○○	◇ boraceus	calx ♄ et viride ♀	smaragdus artif.	calx ♂	encaustum fusco-rubrum	et ▽	volatile
				calces ♄ et cobalt	saphyrus artif	calc. metal. combinat.	encaustæ gradjuati mixt color		aer varius ut ♃
				calces cobalti et ☉	amethyste ☉ et calx cobalti artif.		spec. lap. lazuli art.	÷△ &a	△◑ △◑ △◑ &a
				calces ♄ et ♂	Hyacinth artif.	porcelana minus alba	incrustatio alba porcelanæ	▽ ▽ et	○○○ ☌
				calces ♄ et ♃	opalum encaustum album	vasa figulina	incrustatio vas. figul. fayence	▽ et vegetabile	♄
				Kaolin gypsum	porcelana porcelana reaumur	☉	incrustatio ☉	substiæ incognitæ	sp. rectors odores
				argilla ♉ cois	vasa figu-=lina sonora	♀	incrustatio ♀	÷▽	÷▽ berolinense
				☉	crystallus incrust. per ☉			A	△ ☌ phogisti catus
				☉ et calc. coloratæ	aventuri-=na var. color.				

Double decomposition

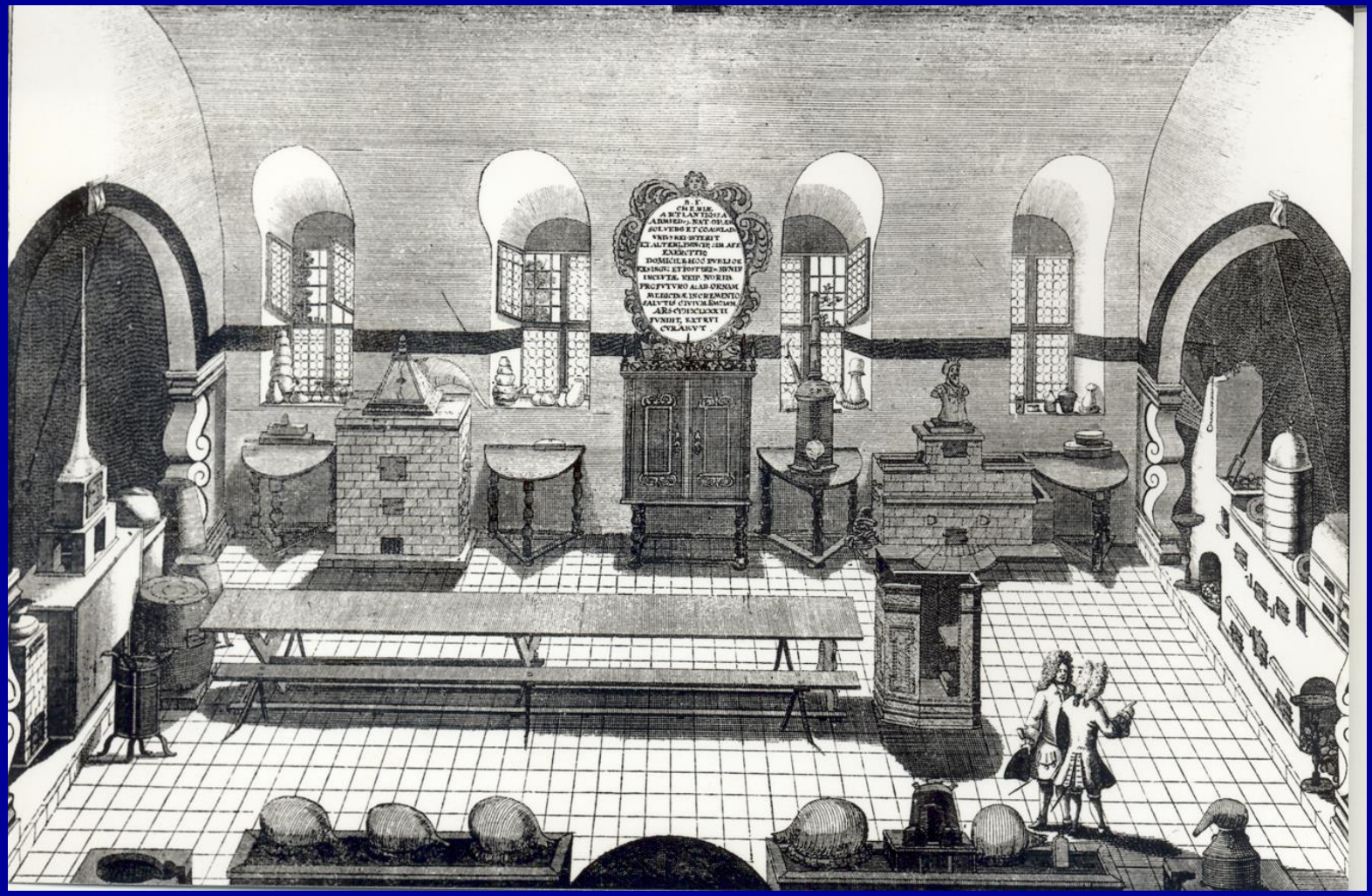
- AB + CD => AD + BD
- A, B, C, D are outcomes of chemical analysis; but whether they are truly ‘elemental’ in the modern sense is not immediately clear
- Also Lavoisier’s definition does not offer a solution. Examples: Cl seen as an oxygen compound; or CN as an element.
- See: F.L. Holmes, *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, 1989).

Chemical Revolution (late 18th C)

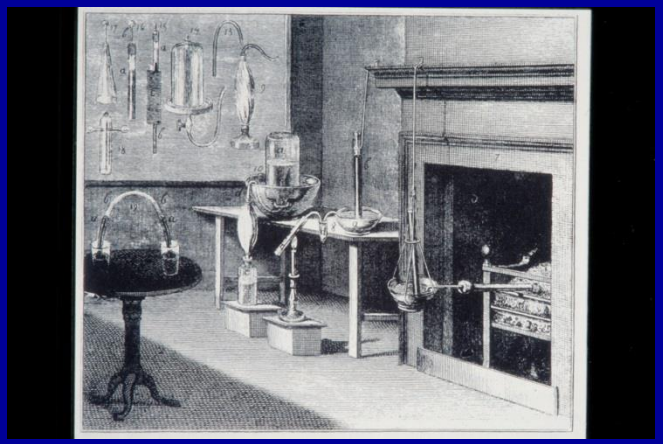
- **Narrow sense:**
- Replacement phlogiston theory by Lavoisier's chemistry
- Based on quantitative methods
- And binary, systematic nomenclature

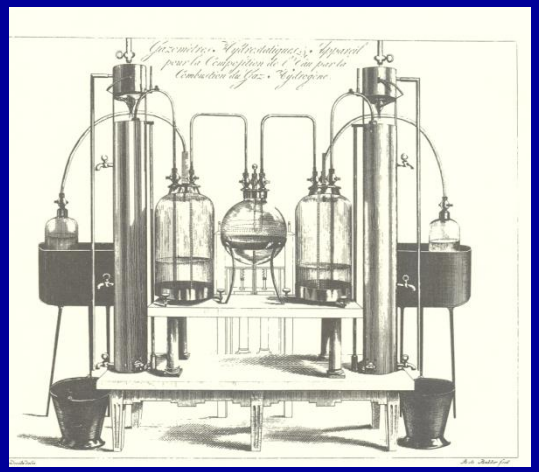
- **Broader sense (the above +):**
- Improved knowledge of double decomposition
- Introduction of new analytical techniques (reagents; volumetrics; gas chemistry
- 'Revolution' of the chemical laboratory
- Paleotechnic revolution in the chemical industry (from wood to coal; from organic feedstocks to minerals)

‘Old laboratory’: University of Altdorf: teaching the ‘fire art’ (1680)
N.B. ‘industrial workshops’ were quite similar

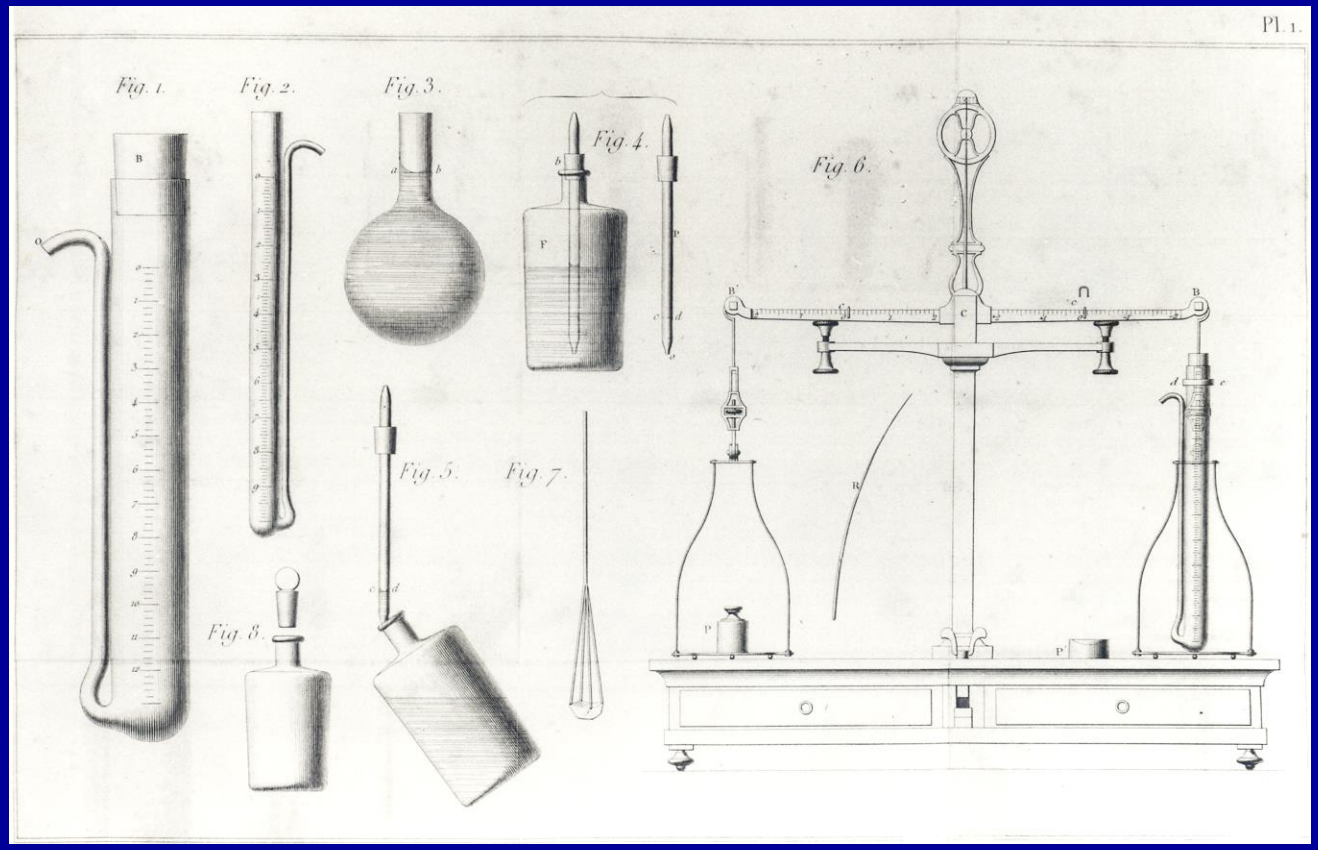


Manipulation of gases: Priestley 1774; Van Marum 1790; Mr. & Mrs. Lavoisier 1790





Volumetric methods (Descroizilles; Gay Lussac)



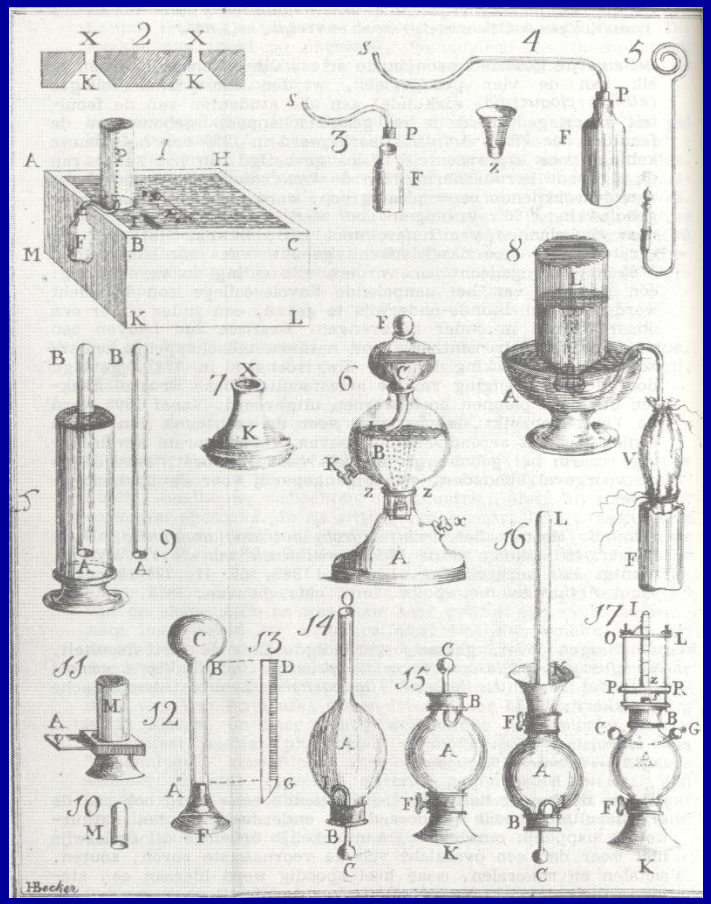
Use of the blow-pipe by Cronstedt (1757) and reagents by Bergman (c1770)

‘New laboratory’ Uni Giessen (1842)

1770-1830

- (a) scaling-up of industry
- (b) scaling-down of laboratory practices
- Result: the united material culture between chemistry and industry breaks down.
- But: introduction of new chemical theories in industry

(2) 1770-1830



Example: White lead

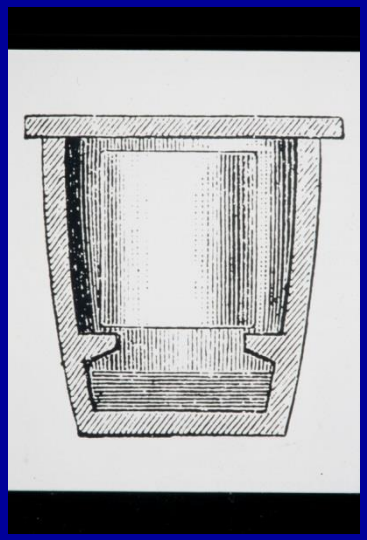
- White lead is basic lead carbonate, approximately 2 $PbCO_3.Pb(OH)_2$, but in practice with quite some variation in composition, and in several crystal modifications.

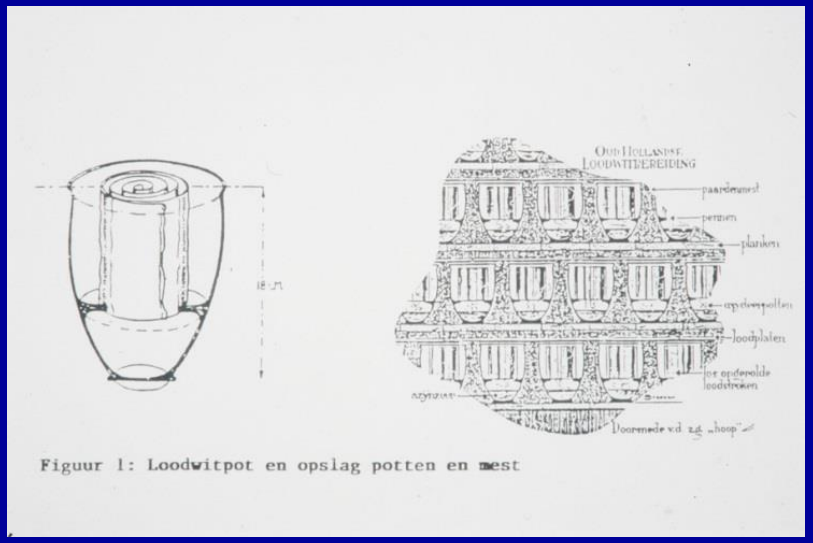
- A crucial pigment used by the great painters of the 17th century (Rembrandt, etc.); but also very common in painting of ships, wooden houses, etc. Very good covering power.

- 'Dutch process', developed in the 16th century dominated the European industry. Virtual monopoly of the Netherlands; but some competition from Britain since the 17th C, and Germany, Austria and later France since the 18th C.

White lead (ceruse)

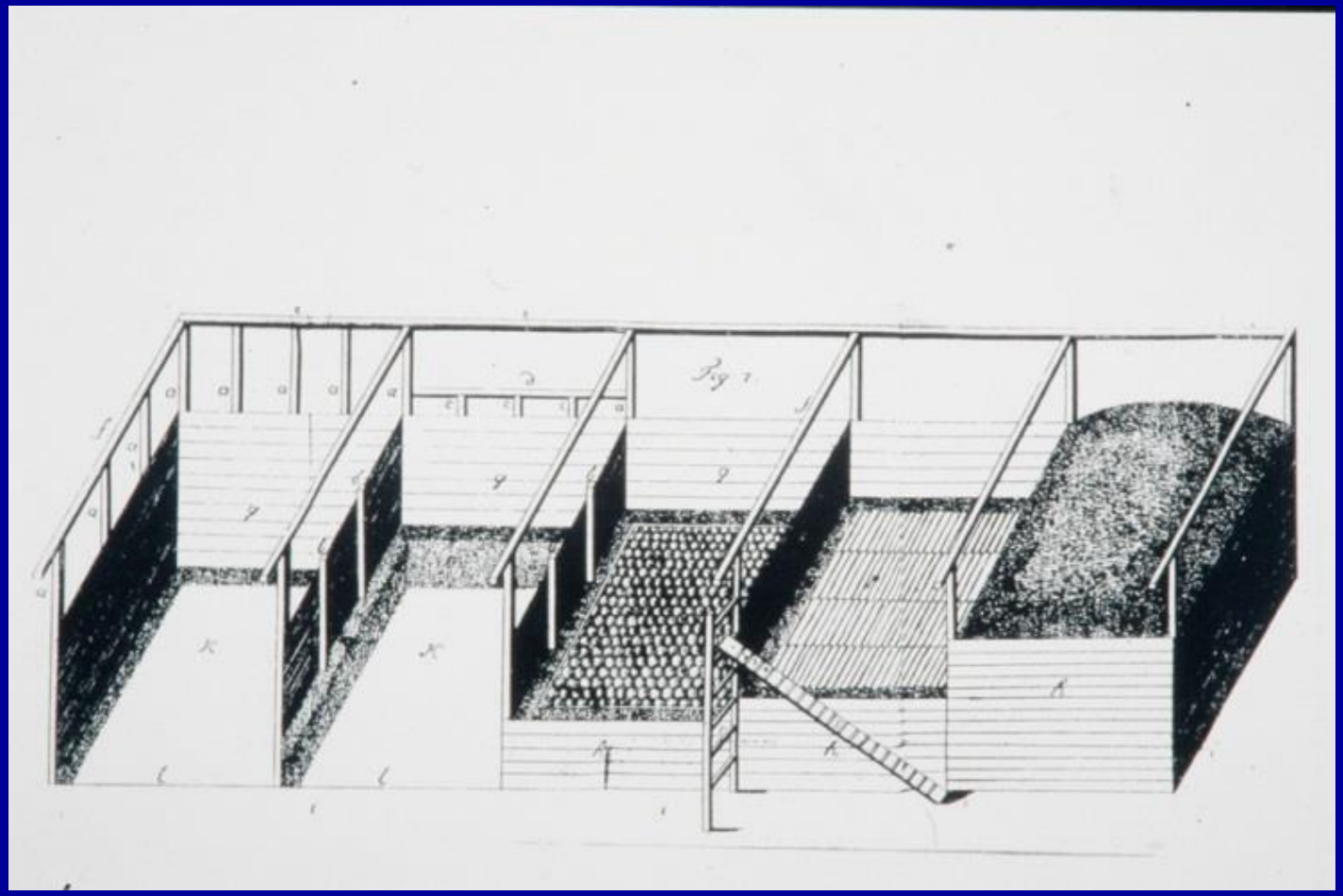
- Lead sheets are rolled into coils
- Placed in pots over vinegar
- Convered by sheets of lead
- The pots placed in stacks, in beds of horse dung
- Ca. 700 pots in one layer
- Several thousands of pots in one stack
- Horse dungs starts fermenting
- Temperature in the stack may rise to 70 centigrade
- After 6-10 weeks the sheets are totally corroded, and the stack is dismantled.



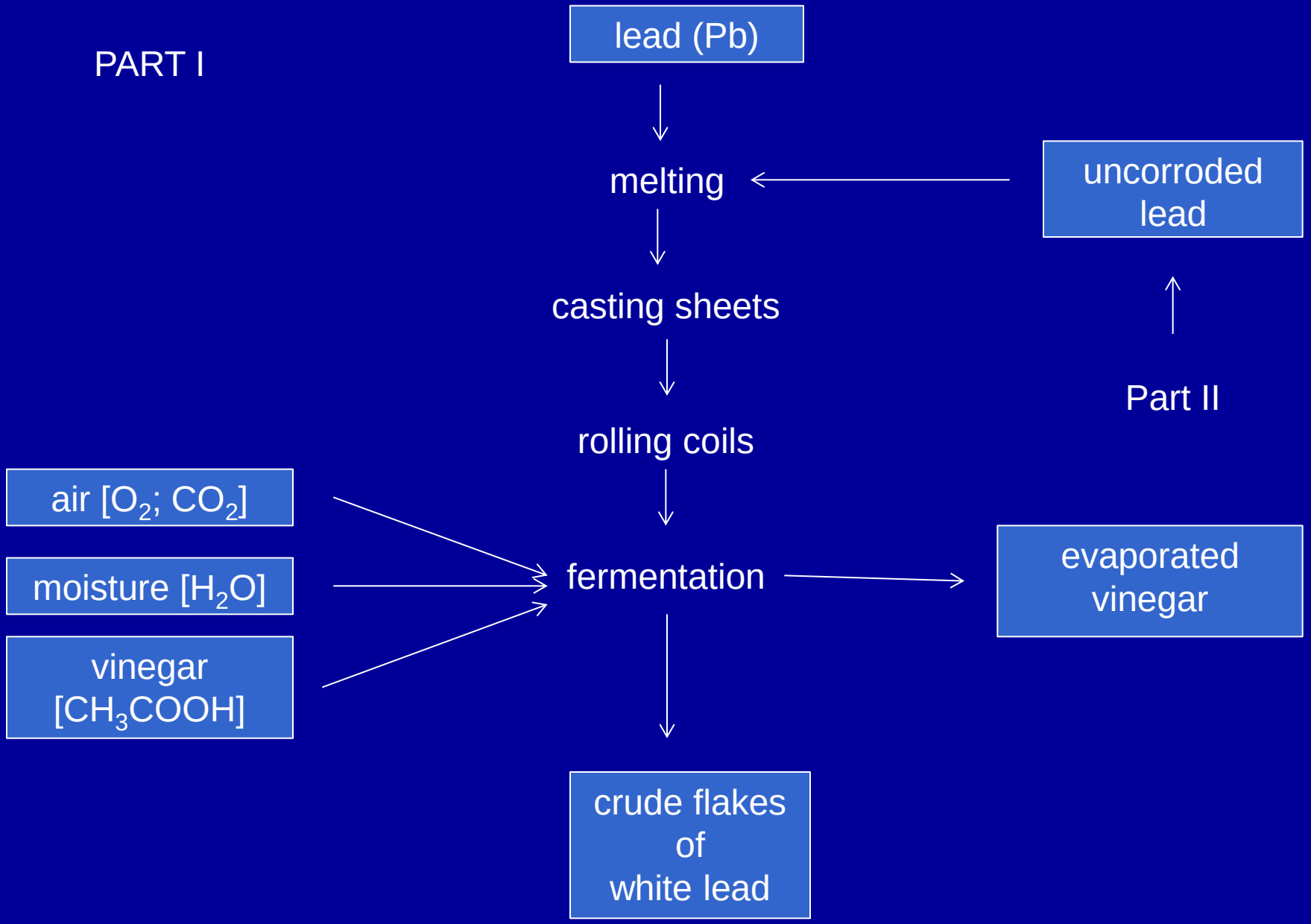


Figuur 1: Loodwitpot en opslag potten en mest

Construction of a stack



PART I


lead (Pb)
melting
uncorroded lead
casting sheets
Part II
rolling coils
air [O_2; CO_2]
moisture [H_2O]
vinegar [CH_3COOH]
fermentation
evaporated vinegar
crude flakes of white lead

Traditional chemical understanding of the process

- According to the ideas of Stahl:

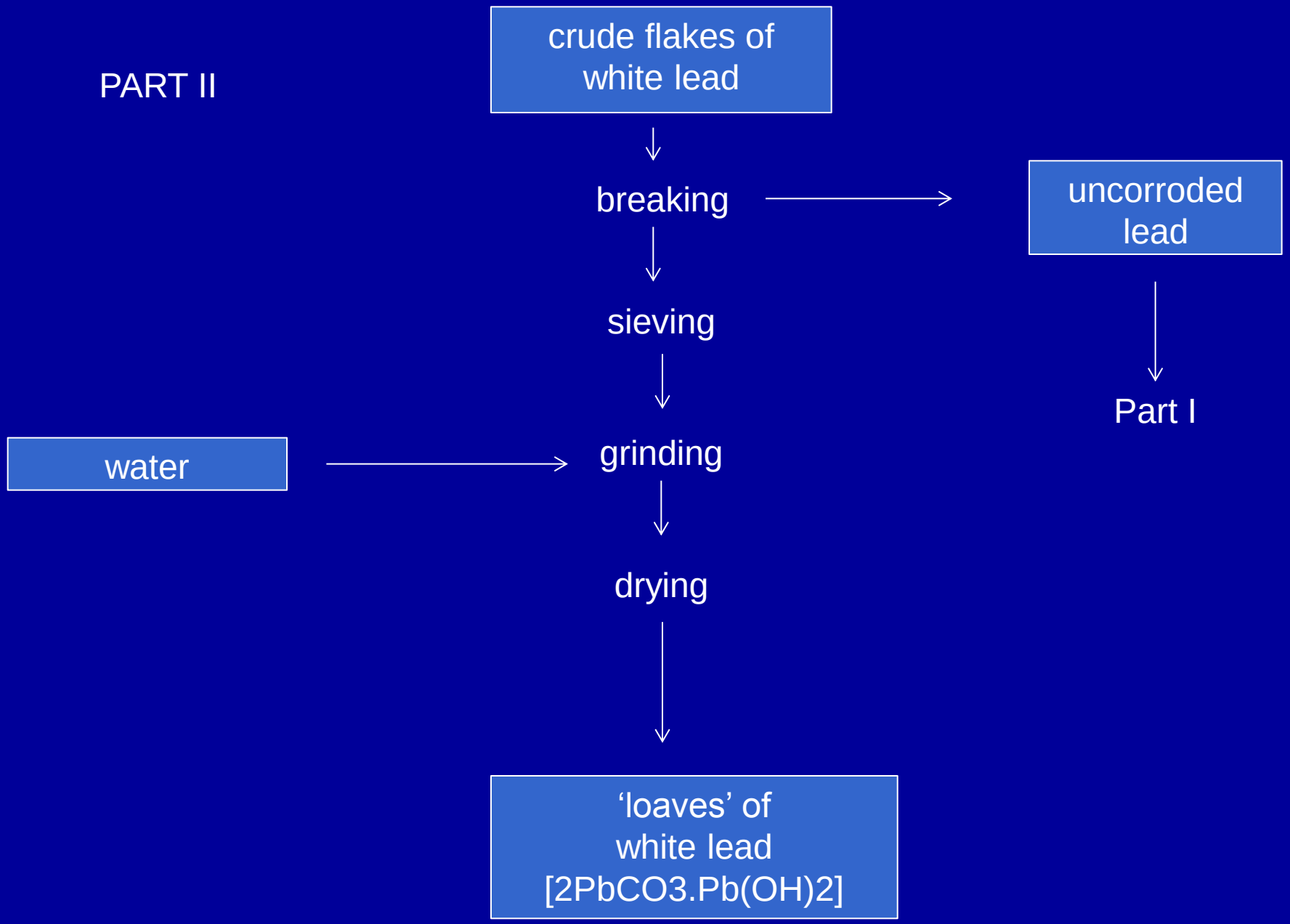
lead + vinegar => ‘calx of lead’ + ‘phlogistinated vinegar’

(i.e. corrosion of lead with the help of acids, in particular vinegar)

‘Refining’ the crude white lead flakes

- Separation of white lead from uncorroded lead by breaking, sieving and grinding
- Very toxic: high mortality rates among the white lead workers
- Organic inputs: vinegar and horse dung; and wind power

PART II


crude flakes of white lead
breaking
uncorroded lead
Part I
sieving
water
grinding
drying
‘loaves’ of white lead [2PbCO3.Pb(OH)2]

Impact of the ‘chemical revolution’ on the white lead industry

- research on gases – the composition of air
- 1756 Joseph Black discovers ‘fixed air’ (CO_2)
- 1773 Torbern Bergman publishes on the ‘Acid of Air’ (CO_2), and discovers that white lead is compound of Acid of Air (CO_2) and litharge (PbO)
- Later investigators in the 18th C concluded that white lead is 84% PbO and 16% CO_2

Total reinterpretation of white lead making

- Horse dung = not only a source of heat, but also of CO2
- Oxygen supply is important
- There is no acetate in the final product, so white lead can also be produced without the use of vinegar (= catalyst)
- Most radical: it can be made by double decomposition of any basic carbonate with any soluble salt of lead

So: modern chemistry destroys all restrictions of the old Dutch process

Improvements in the process

- Old Dutch process > New Dutch process, by improving oxygen supply (19th C)
- 1792 Von Herbert in Austria constructs a plant without horse dung: Chamber process = heated chambers + CO2 supply by fermentation of wine lees (and later external supply)
- From 1780 onwards totally new ‘chemical’ processes via double decomposition; first as ‘by-product’ of soda ash production

New ‘chemical’ processes

- c.1770 Carl Wilhelm Scheele (1742-1786) suggests to produce mineral alkali (soda) from sea salt, with the help of litharge (PbO)

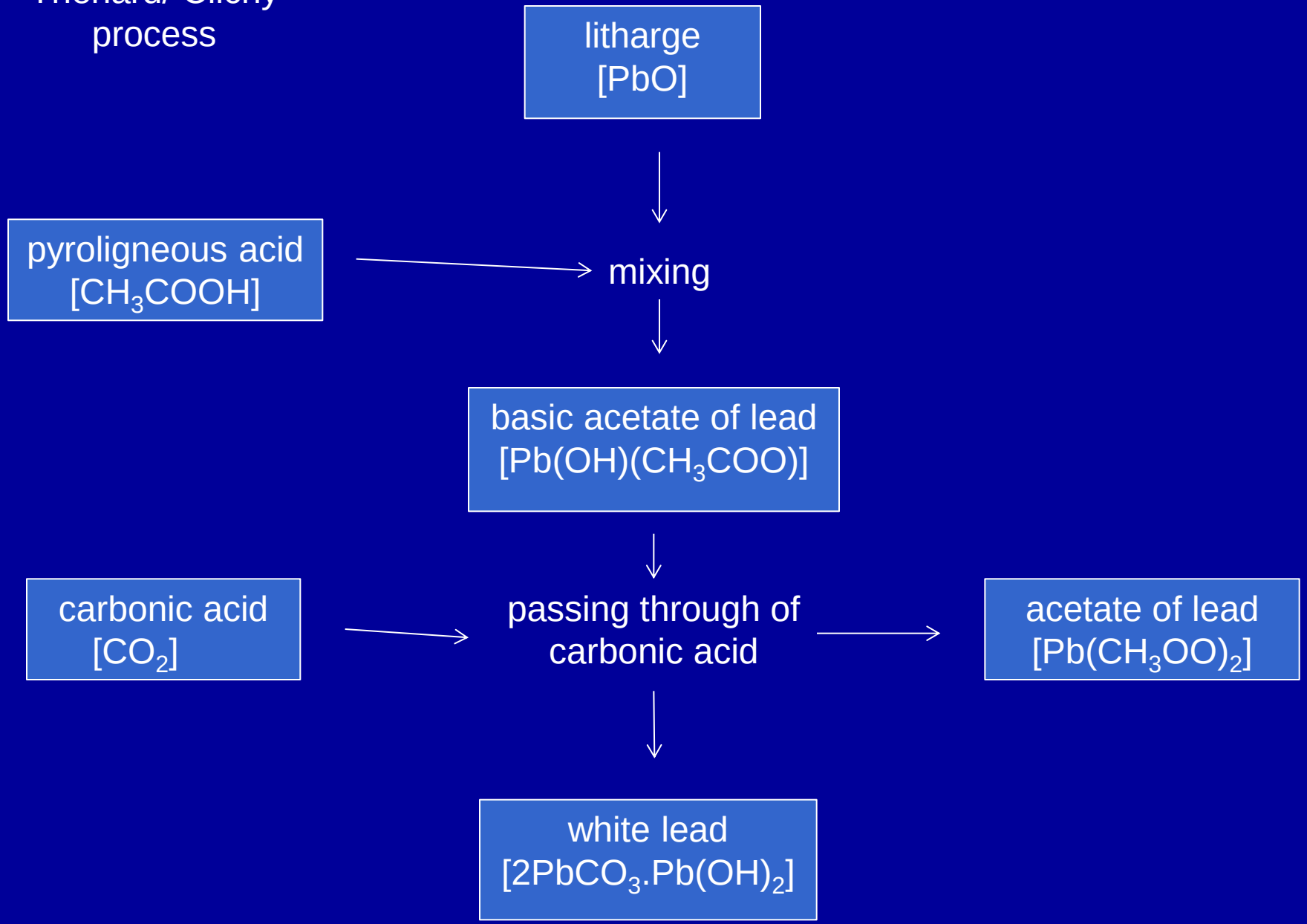
- 1781 James Turner files a patent for the production of a yellow pigment (Turner's yellow), mineral alkali and white lead from sea salt and litharge (yellow via heating of Pb-salts, because mostly PbCl2 was the product)

[2 NaCl + 3 PbO + 3 CO_2 => Na_2CO_3 + 2 $PbCO_3.Pb(OH)_2$ + 2 HCl]

Three variations of the Turner process used in industrial practice:

- Chaptal (c1800): PbCl2 + H2SO4 + carbonate (2-steps) > white lead
- Keir (1806): PbCl2 + alkali + CO2 > white lead
- Cochrane/Dundonald (1796): change process conditions > white lead

Thenard/ Clichy process

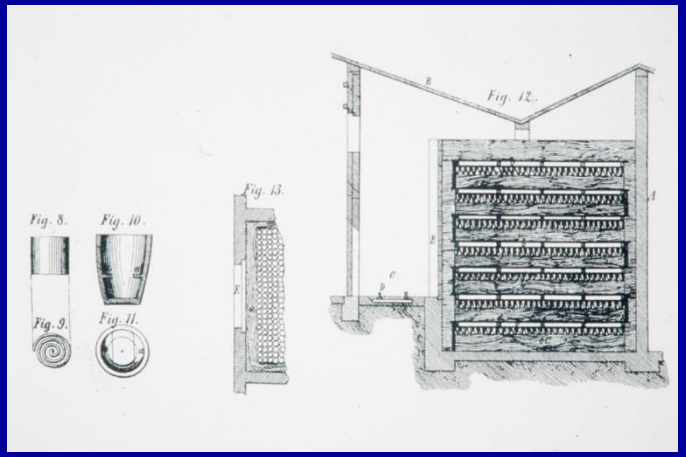


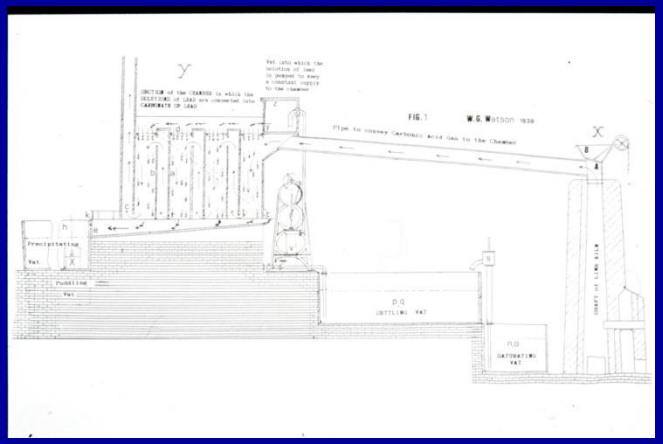
Technological competition: tradition vs. chemistry

- After ca. 1800 many new chemical processes were developed.
- In Netherlands between 1834 and 1867 at least 17 patents + several new factories
- They all failed, just like the new plants in France
- Main problem: coverage by the synthetic lead was less good
- Later understood as too small crystallites
- Also high energy costs: coal for steam engines and CO2 production.

White lead

- Improvement of classical method (CO_2 supply)
- Completely new synthetic methods
- Last ones failed because of lower product quality (crystal size)





Conclusions

- ‘Chemical revolution’ (in the broad sense) completely changed the horizon of the chemical industry by offering many different options.
- Understanding chemical reactions in term of ‘elements’ or, broader defined, ‘constituents’, ‘components’, ‘aggregates’ was a crucial step.
- But chemistry does not determine everything; ‘physics’ (e.g. crystal size) is very important as well. White lead = performance product