INSTITUTE FOR CHEMICAL PROCESSING OF COAL

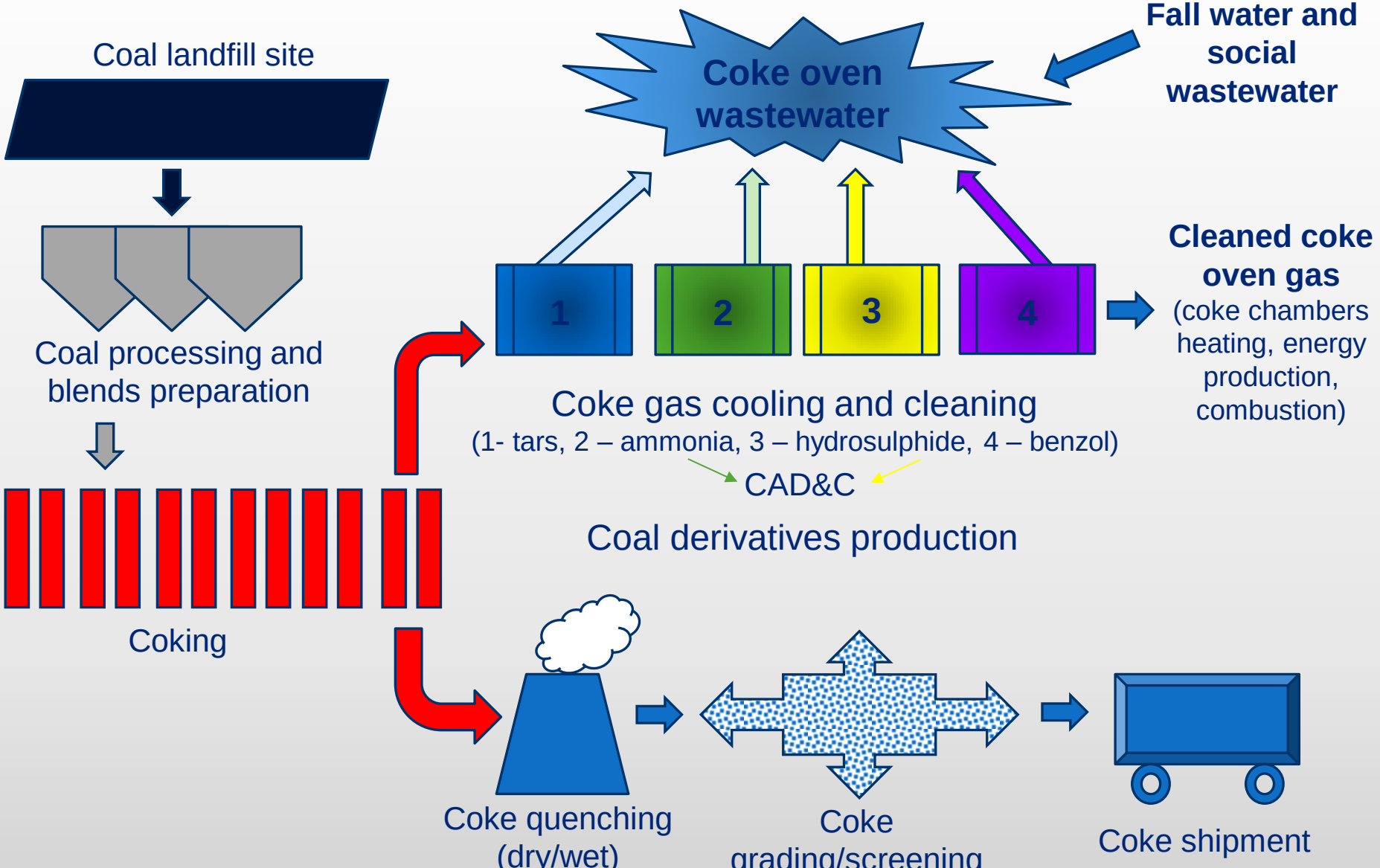
1955-2017

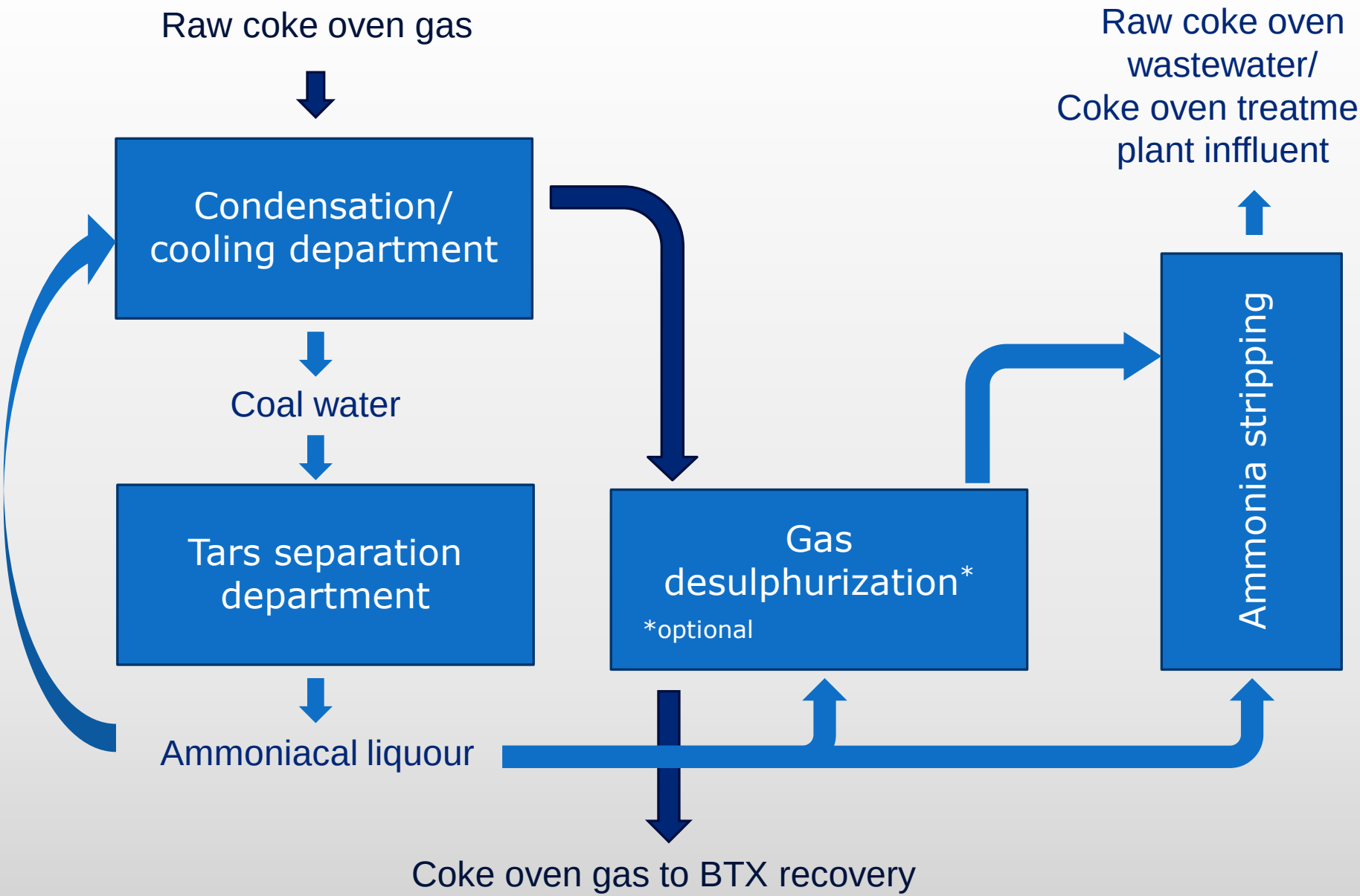
Research Fund for Coal & Steel

Innowatreat

MAIN CONTAMINANTS IN COKE OVEN WASTEWATER – METHODS OF DETERMINATION AND REMOVAL

Anna Kwiecińska, Jan Figa, Katarzyna Rychlewska, Maciej Chrubasik

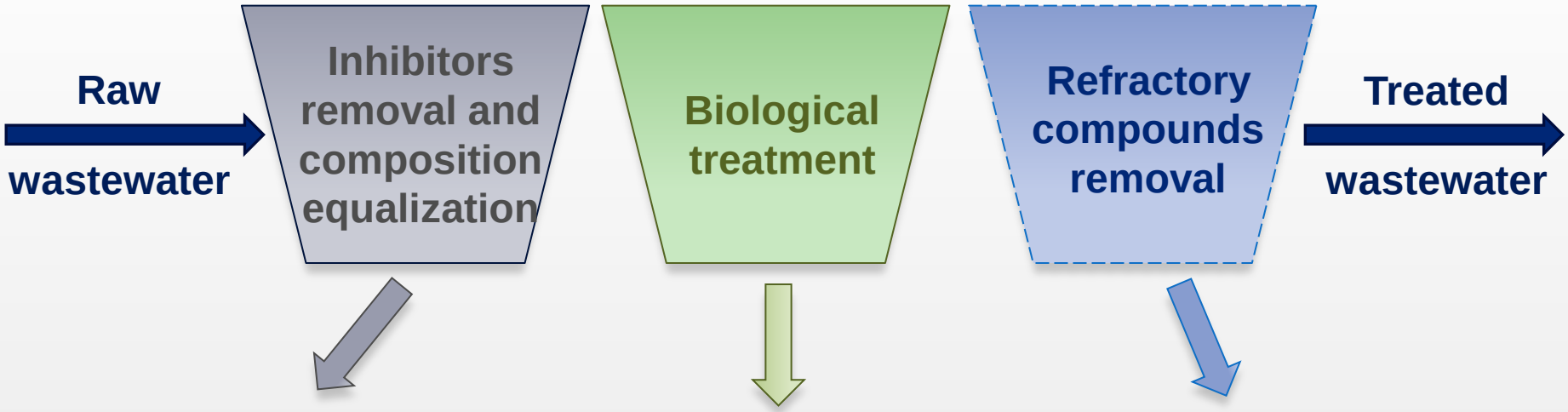

Coke oven wastewater
Fall water and social wastewater
Coal landfill site
Coal processing and blends preparation
1
2
3
4
Cleaned coke oven gas
(coke chambers heating, energy production, combustion)
Coke gas cooling and cleaning
(1- tars, 2 – ammonia, 3 – hydrosulphide, 4 – benzol)
CAD&C
Coal derivatives production
Coking
Coke quenching (dry/wet)
Coke grading/screening
Coke shipment


Raw coke oven gas
Condensation/ cooling department
Coal water
Tars separation department
Ammoniacal liquour
Gas desulphurization*
*optional
Ammonia stripping
Raw coke oven wastewater/ Coke oven treatment plant inffluent
Coke oven gas to BTX recovery

Wastewater is generated at an average rate ranging from **0.3 to 4** m^3 per ton of coke

Parameter	Unit	Concentration in influent	BAT conclusion	National standards
pH	-	7-9.5	n/d	n/d
Spec. cond.	µS/cm	5 000-12 500	n/d	n/d
COD	mgO_2/dm^3	2 400-4 200	<220	<250
BOD_5	mgO_2/dm^3	500-1 500	<20	<25
Tars	**mg/dm^3**	**5-150**	**<0.05**	**n/d**
Sulphides	**mg/dm^3**	**10-50**	**<0.1**	**<0.2**
Cyanides (WAD)	**mg/dm^3**	**5-20**	**<0.1**	**<0.1**
Cyanides (complex)	**mg/dm^3**	**-**	**n/d**	**<5**
Thiocyanates	**mg/dm^3**	**50-420**	**<4.0**	**<10**
Phenols	**mg/dm^3**	**150-1 200**	**<0.5**	**<0.1**
Ammonia	**mg/dm^3**	**120-790**	**<15-50 ($N_{inorg.tot}$)**	**<10 $N\text{-}NH_4$ <30 N_{tot}**

Coke oven wastewater treatment



MECHANICAL METHODS
- Sedimentation
- Flotation
- Filtration

CHEMICAL METHODS

REMOVAL OF TARS, SULPHIDES, CYANIDES

AMONIFICATION

NITRIFICATION

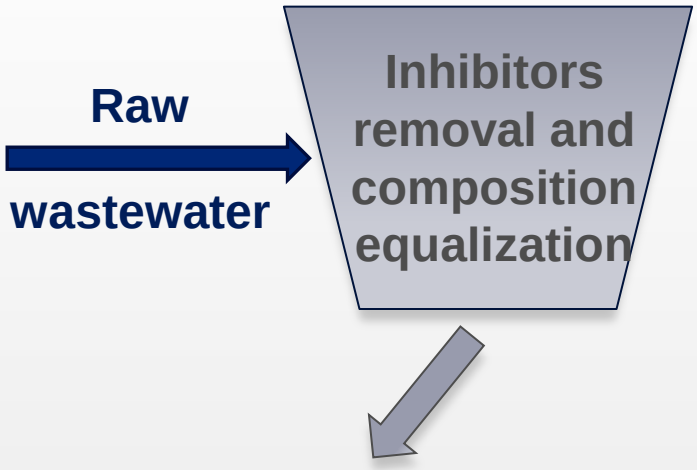
DENITRIFICATION

OXIDATION

REMOVAL OF AMMONIA AND PHENOLS

MULTIFICTIONAL REACTORS
- Activated carbon adsorption
- Coagulation
- AOPs

POLISHING – COD AND CYANIDES



MECHANICAL METHODS
- **Sedimentation**
  - **Flotation**
  - **Filtration**

CHEMICAL METHODS

REMOVAL OF TARS, SULPHIDES, CYANIDES

At all coke oven plants chemical loop is operated with the use of iron (ferrous of ferric) salts

Mechanisms

Tars – coagulation

Cyanides
Complexation
$Fe^{2+/3+} + 6CN^{-} \rightarrow Fe(CN)_6^{4-/3-}$
Precipitation
$Fe^{2+/3+} + Fe(CN)_6^{4-/3-} \rightarrow Fe_x[Fe(CN)_6]_y$

Sulphides
Precipitation
$Fe^{2+} + S^{2-} \rightarrow FeS$
$Fe^{3+} + S^{2-} \rightarrow Fe_2S_3 \rightarrow FeS + S^0$

Most national coke oven plant operates with the use of nitrification/denitrification loop;

Biological treatment

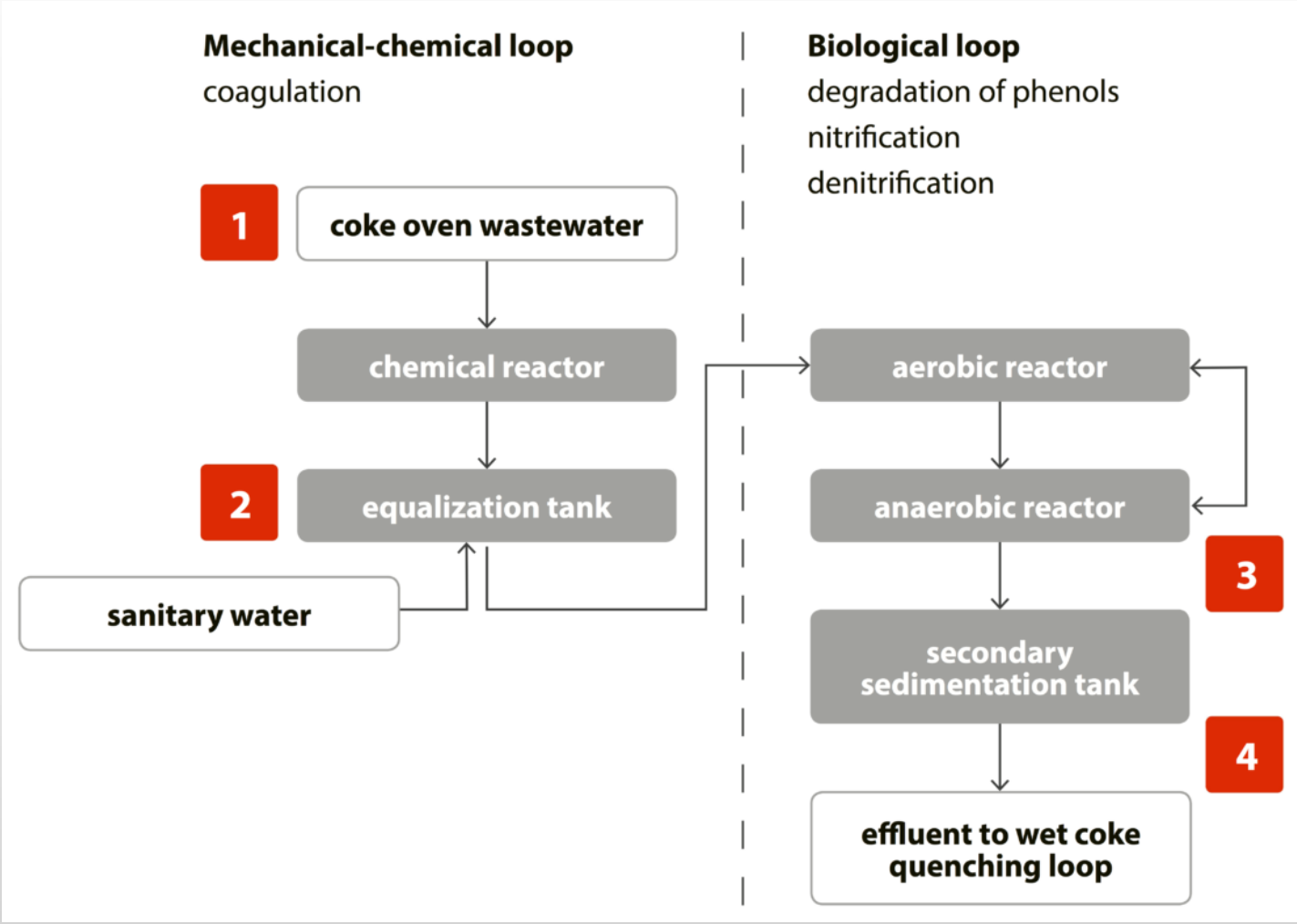
AMONIFICATION

NITRIFICATION

DENITRIFICATION

OXIDATION

REMOVAL OF AMMONIA AND PHENOLS



…beyond standards!

Only one plant is equipped with amonification process;

Biological treatment

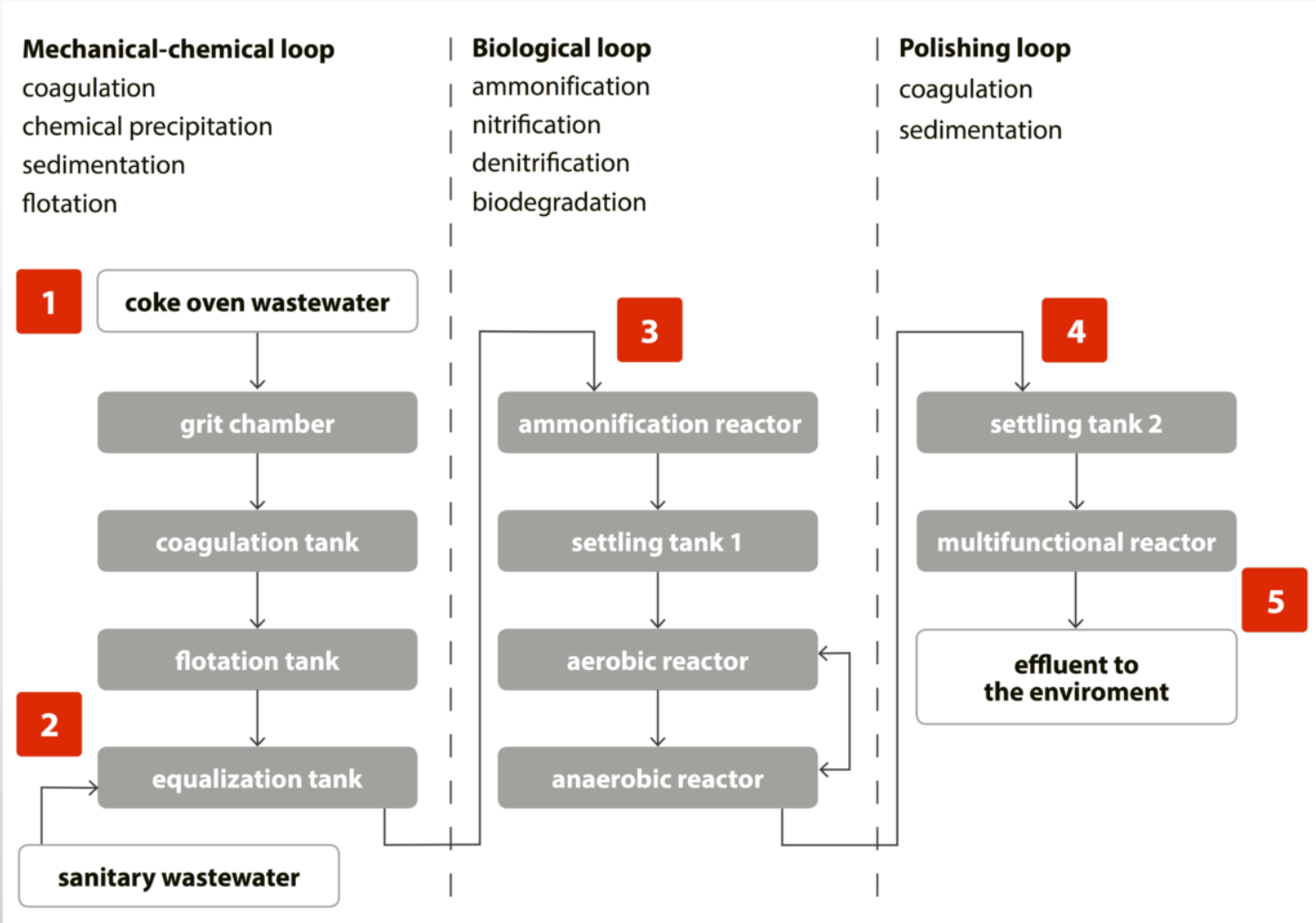
AMONIFICATION

NITRIFICATION

DENITRIFICATION

OXIDATION

REMOVAL OF AMMONIA AND PHENOLS



…beyond standards!

But combined arrangement can also be found;

Biological treatment

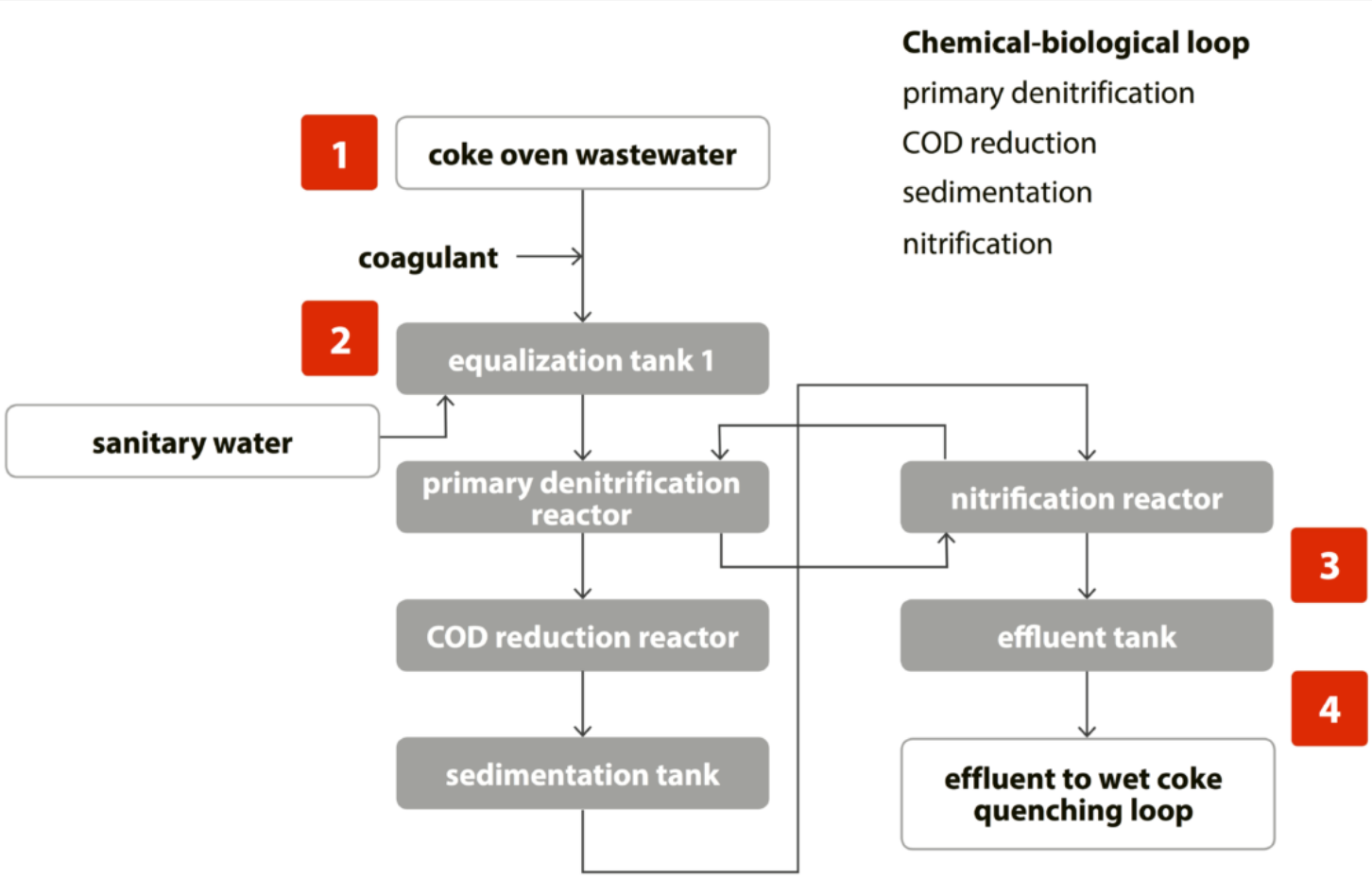
AMONIFICATION

NITRIFICATION

DENITRIFICATION

OXIDATION

REMOVAL OF AMMONIA AND PHENOLS



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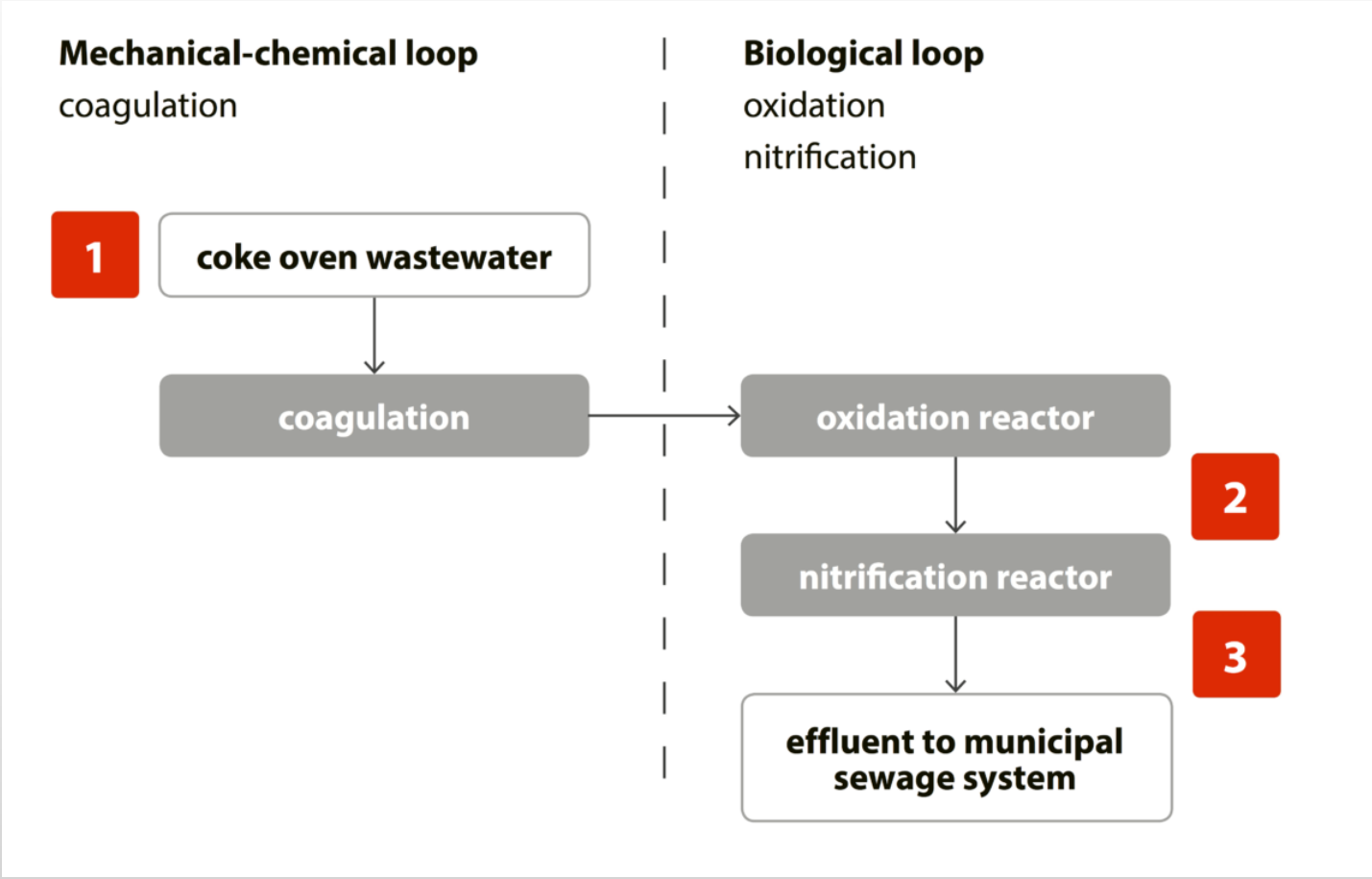
DENITRIFICATION

OXIDATION

REMOVAL OF AMMONIA AND PHENOLS



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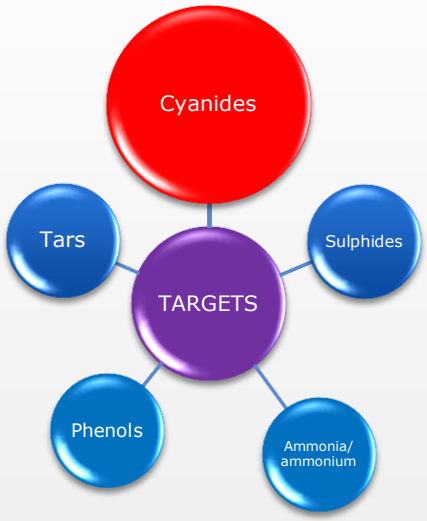


Two analytical groups: easily liberatable and complex.

Easily liberatable: free cyanides (CN^-, HCN) and weak metal-cyanide complexes (WADs);

Complex: strong metal-cyanides complexes (ca. $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$).

Sample preservation

addition of NaOH increase sample pH above 10 – 24 hours.

addition of NaOH and $ZnSO_4$ - 7 days (formation of ZnCN complex – WADs recovery required).

Recovery

Free – not required

WADs – (1) combined distillation and air stripping for 1 h at the presence of H_3PO_4 and dedicated buffer solution; (2) air stripping at pH = 4 and room temperature carried out for 4 h. (1)&(2) released HCN caught in washers with NaOH.

Complex/total* - (1) acidification with H_2SO_4 at presence of Hg and Mg catalysts. Next, distillation combined with air stripping run for 1 h; (2) distillation combined with air stripping at presence of HCl and Cu catalyst run for 1 h; (1)&(2) released HCN caught in washers with NaOH.

(*) if a sample after WADs recovery is used – complex, if fresh sample is used - total

Cyanides analysis

No	Method	Range of CN^- conc. without dilution	Preliminary treatment*	Equipment	Recom-mendation
1	Colorimetric benzidine-pyridine method	0.01-1.0 mg/dm^3	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	No
2	Titrimetric argentometric method	above 1 mg/dm^3	No	Laboratory glass Set of reagents	No
3	Colorimetric barbituric-pyridine method	0.01-1.0 mg/dm^3	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
4	HACH Lange LCK 315	0.01-0.6 mg/dm^3	Yes	Distillation set Dedicated tests Spectrophotometer	Yes
5	HACH Lange LCK 319	0.03-0.35 mg/dm^3	No	Dedicated tests Spectrophotometer	Yes
6	Potentiometric method with the use of argentometric titration	0.05-100 mg/dm^3	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	Yes
7	Ion Chromatography analysis with Pulsed Amperometric Detection	0.05-5 mg/dm^3	No	Ion chromatograph AS-7 analytical column Silver working electrode	Yes
8	Continuous flow analysis with photometric or amperometric detection	0.002-0.5 mg/dm^3	No	Dedicated device Set of reagents	Yes

Two analytical groups: easily liberatable and insoluble.
Easily liberatable: free sulphides (S^{2-}, HS^-, H_2S), weak acid soluble (WASs)
Insoluble: IInd analytical group (Cu, Bi, Sn, Cd, As, Sb)

Sample preservation
addition of NaOH increase sample pH above 10 – 4 hours.
addition of NaOH and $Zn(CH_3COO)_2$ – 3-4 days (analysis at acidic conditions).

Recovery
Free – not required
WASs – (1) thermal distillation at presence of H_2SO_4 solution accompanied with inert gas stripping; (2) inert gas stripping with the use of acidic buffer solution.
(1)&(2) released HCN caught in washers with $Zn(CH_3COO)_2$.
Insoluble* - no standards or limitations found.

Sulphides analysis

No	Method	Range of S^{2-} conc. without dilution	Preliminary treatment	Equipment	Recom-mendation
1	Colorimetric method for water soluble and acid soluble sulphides with p-aminodimethylaniline	up to 20 mg /dm^3	No	Laboratory glass Set of reagents	No
2	Iodometric method for water soluble and acid soluble sulphides	> 1 mg/dm^3	Yes	Laboratory glass Set of reagents	No
3	Colorimetric method for water soluble sulphides with HMB and thiofluoroscein	0.005-0.04 mg/dm^3	No	Laboratory glass Set of reagents	No
4	Photometric method for water soluble and acid soluble sulphides with methylene blue formation	0.04-1.5 mg/dm^3	Yes	Laboratory glass Set of reagents Spectrophotometer	Yes
5	HACH Lange LCK 653	0.1-2.0 mg/dm^3	Yes	Distillation set Dedicated tests Spectrophotometer	Yes
6	Potentiometric method for water soluble sulphides analysis with argentometric titration	0.05-100 mg/dm^3	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	Yes
7	Ion Chromatography analysis for water soluble sulphides with Pulsed Amperometric Detection	0.05-5 mg/dm^3	No	Ion chromatograph AS-7 analytical column Silver working electrode	Yes

Two groups: free and fixed.

Free: NH_4OH, $(NH_4)_2CO_3$, NH_4HCO_3, $(NH_4)_2S$, NH_4CN

Fixed: NH_4Cl, NH_4SCN, $(NH_4)_2S_2O_3$, $(NH_4)_2SO_4$

Two forms: NH_3 (pH>8), NH_4 (pH<7) – analytical results recalculation to NH_4

Sample preservation

As soon as possible, but in general up to 7 days not required.

Recovery

In some methods for ammonia determination, the need for ammonia recovery by means of distillation can be met. However, we investigated mostly methods, in which the preliminary treatment of sample is not required or is a part or determination mechanism.

Ammonia analysis

No	Method	Range of NH_4 conc. without dilution	Preliminary treatment	Equipment	Recom-mendation
1	Direct Nesslerization	Depends on the concentration of standard solution used for calibration	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	No
2	Ion-selective method for ammonia determination	0.5-1000 mg/dm^3	No	Laboratory glass Set of reagents Dedicated electrodes Laboratory multimeter	No
3	Distillation method with titration	up to 100 mg/dm^3	No	Distillation set Laboratory glass Set of reagents	Yes
4	Manual spectrometric method	up to 1 mg/dm^3	No	Laboratory glass Set of reagents Spectrophotometer	No
5	HACH Lange LCK 302, 303, 304, 305	0.015-130 mg/dm^3	No	Dedicated tests Spectrophotometer	Yes
6	Ion chromatography with conductometric detector	0.1-10 mg/dm^3	No	Ion chromatograph Analytical column Conductometric detector	Yes
7	Flow analysis method (FIA and CFA) with spectrometric detection	0.1-10 mg/dm^3	No	Dedicated device Set of reagents	Yes

Analytical definition.

Aromatic compounds with at least one hydroxide group. Due to the appearance of multiple compounds, which can be defined as phenols, so called “phenol index determination” has been established. It corresponds to all compounds present in the sample, which in mechanism of determination react in the same way as phenol does.

Sample preservation

Unpreserved – 4 h

Acidification to pH = 4 with H_3PO_4 and addition of $CuSO_4$ (1 g of $CuSO_4x5H_2O$ per 1 dm^3 of sample) – 7 days

We found, at such high levels, the preservation is not required

Recovery

In some methods for phenols determination, the need for recovery by means of distillation can be met.

Phenols analysis

No	Method	Range of phenols conc. without dilution	Preliminary treatment	Equipment	Recom-mendation
1	4-aminoantipyrine method with chloroform extraction	0.001-1.0 mg/dm^3	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
2	4-aminoantipyrine method without chloroform extraction	0.1-50 mg/dm^3	Yes	Distillation set Laboratory glass Set of reagents Spectrophotometer	Yes
3	Bromometric method for phenols determination	>10 mg/dm^3	Yes	Distillation set Laboratory glass Set of reagents	No
4	HACH Lange LCK 345	0.05-5 mg/dm^3	No	Dedicated tests Spectrophotometer	Yes
5	Gas chromatography with flame ionization detector or mass spectrometer	0.1-100 mg/dm^3	No	Gas chromatograph PEG capillary column (Stabilwax) Flame ionization detector or Mass spectrometer	Yes
6	Phenols determination by flow analysis	0.01-1 mg/dm^3	No	Dedicated device Set of reagents	Yes

Analytical definition:

6 Borneff PAHs: fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[123cd]pyrene, benzo[ghi]perylene

Sample preservation

Not required

Recovery

(1) Solid phase extraction (SPE) followed by desorption with acetone and benzene.

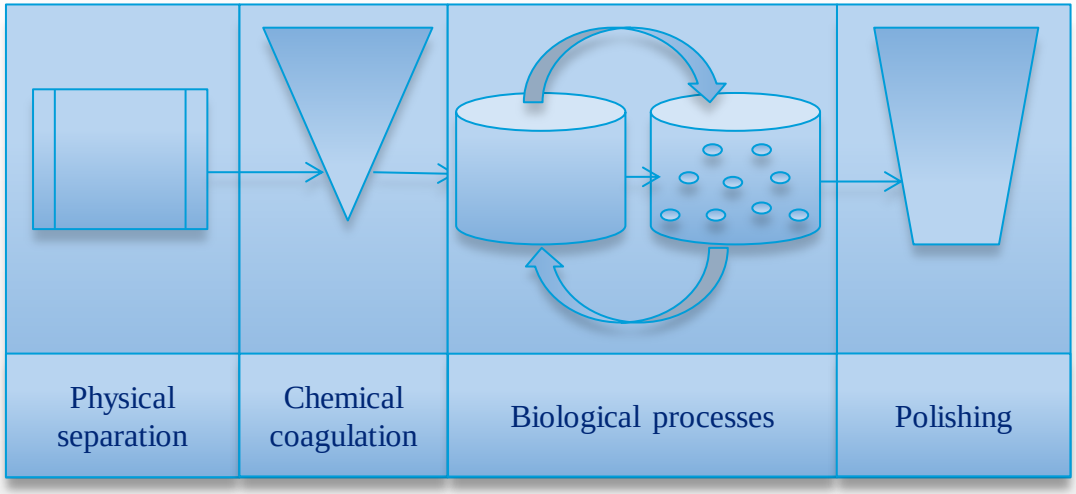
(2) Liquid-liquid extraction (n-hexane, benzene or dichloromethane) – emulsification appearance

(3) Solid phase microextraction – adsorbance of the target compounds on a fiber covered with nonpolar sorbent. Desorption method requires insertion of the fiber into chromatograph injector, where thermal desorption takes place. Low (ng) concentration levels.

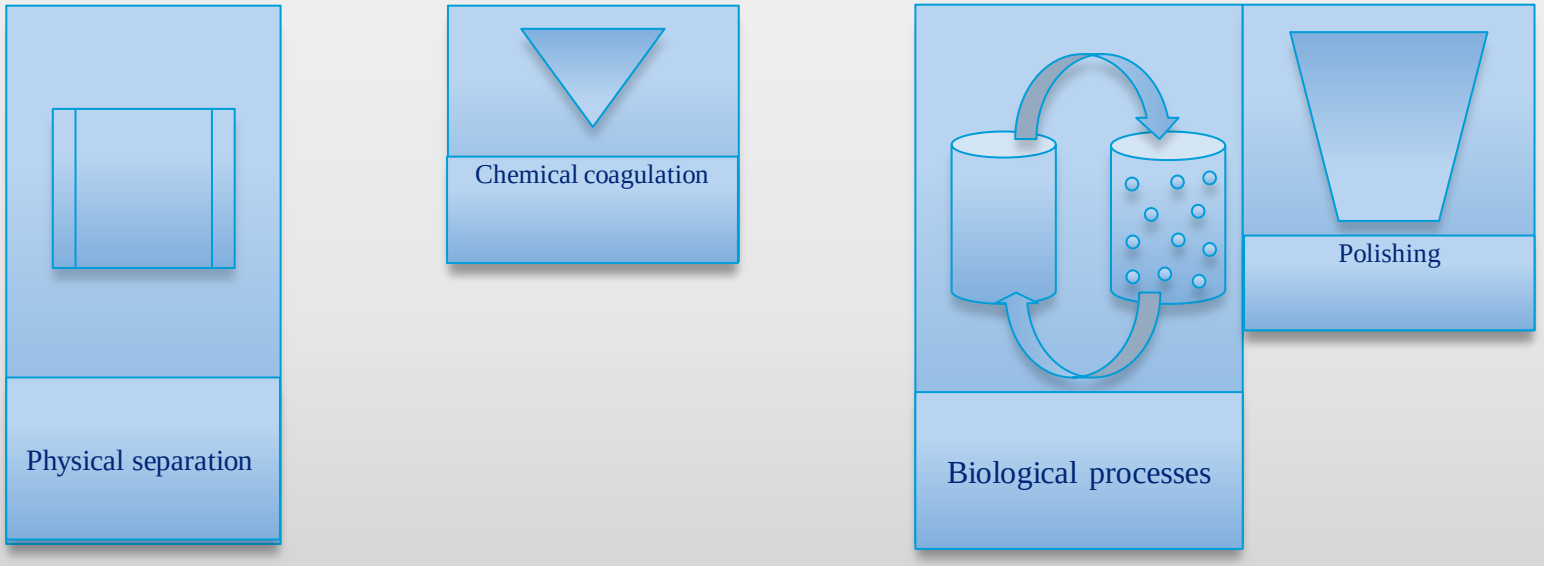
Tars analysis

No	Method	Range of PAHs conc. without dilution	Preliminary treatment	Equipment		Recom-mendation
1	Gas chromatography coupled with flame ionization detector	0.02 – 100 mg/dm^3	Extraction with organic solvents	Laboratory glass	Gas chromatograph Apolar capillary column (Rxi-5) Flame ionization detector	No
			Solid phase extraction	SPE cartridges		Yes
			Solid phase microextraction	Micro-syringe with attached SPME wire		No
2	Gas chromatography coupled with mass spectrometry	0.001 – 10 mg/dm^3	Extraction with organic solvents	Laboratory glass	Gas chromatograph Apolar capillary column (HP-5ms) Quadruple mass spectrometer	No
			Solid phase extraction	SPE cartridges		Yes
			Solid phase microextraction	Micro-syringe with attached SPME wire		No
3	High pressure liquid chromatography coupled with ultraviolet detector	0.02 – 100 mg/dm^3	Extraction with organic solvents	Laboratory glass	High pressure liquid chromatograph Apolar analytical column (C-18) Ultraviolet detector	No
			Solid phase extraction	SPE cartridges		Yes

- **One of the most complex and problematic industrial wastewater – many researches,**
- **Sharpening of environmental and coke quality standards,**
- **Conventional systems are the basis of every research,**
- **Main priorities:**
  - Cyanides removal improvement,
  - Biological processes enhancement,
  - Salts load decrease,
  - Technological grade water recovery.



Conventional system



INNOWATREAT

ACKNOWLEDGEMENT

INNOWATREAT – The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies
"This project has received funding from the Research Fund for Coal and Steel under grant agreement No 710078".

PROJECT CONSORTIUM

EUROPEAN COMMISSION
DIRECTORATE-GENERAL FOR RESEARCH & INNOVATION
Industrial Technologies
Coal and steel

GRANT AGREEMENT

NUMBER — 710078 — INNOWATREAT

This **Agreement** ('the Agreement') is **between** the following parties:

on the one part,

the **European Union (EU)** ('the Agency'), under the power delegated by the European Commission ('the Commission'),

represented for the purposes of signature of this Agreement by Head of Unit - Administration and Finance, DIRECTORATE-GENERAL FOR RESEARCH & INNOVATION, Industrial Technologies, Administration and finance, Patrik KOLAR,

and

on the other part,

1. 'the coordinator':

INSTYTUT CHEMICZNEJ PRZEROBKI WEGLA (IChPW), 000025945, established in UL. ZAMKOWA 1, ZABRZE 41 803, Poland, PL6480008765 represented for the purposes of signing the Agreement by Michal JANASIK

and the following other beneficiaries, if they sign their 'Accession Form' (see Annex 3 and Article 56):

2. **POLITECHNIKA WROCLAWSKA (PWR)**, 000001614, established in WYBRZEZE WYSPIANSKIEGO 27, WROCLAW 50370, Poland, PL8960005851

3. **AKVOLUTION GMBH (Akvola)** GMBH, HRB153250B, established in STRASSE DES 17 JUNI 135, BERLIN 10623, Germany, DE291437109

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INSTYTUT CHEMICZNEJ PRZERÓBKI WĘGLA

(Institute for Chemical Processing of Coal)

Zamkowa St. 1 • 41-803 Zabrze, Poland

Phone: **+48 32 271 00 41**
Fax: **+48 32 271 08 09**

E-mail: **office@ichpw.pl**
Internet: **www.ichpw.pl**

Tax ID No. (NIP): **648-000-87-65**
Nat. Business Reg. No. (REGON): **000025945**

CENTRE FOR TECHNOLOGICAL RESEARCH

Office **+48 32 271 00 41 ext. 300**
Centre Director **+48 32 271 00 41 ext. 143**
e-mail: cit@ichpw.pl

CENTRE FOR LABORATORY RESEARCH

Office **+48 32 271 00 41 ext. 200**
Centre Director **+48 32 271 00 41 ext. 113**
e-mail: cba@ichpw.pl