Co-processing of alternative fuels and raw materials and treatment of organic hazardous wastes in Cement kilns – International experiences and best practice

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Co-processing practice

Co-processing of wastes as alternative fuels and raw materials (AFR) for energy and material recovery has been practiced in the cement industry for 40 years.

Petroleum cokes, a wide range of AFRs and organic hazardous wastes are today used and treated on a regular basis in the cement industry around the world.

Types of co-processing

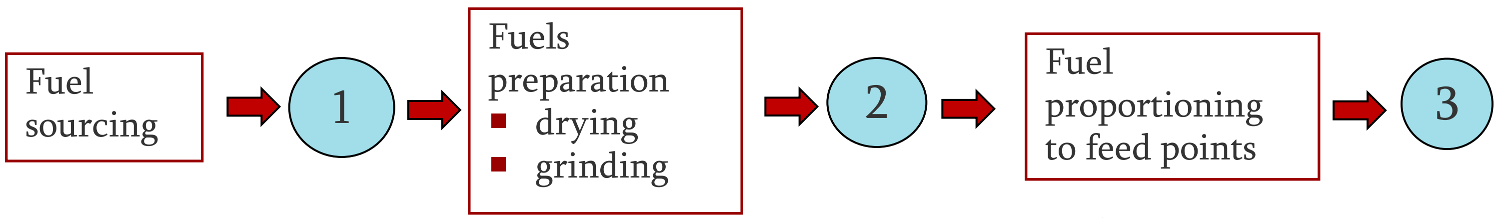
Waste	Substitution	Examples
Energy content (carbon, hydrogen) → Energy recovery	▪ substitution of fossil energy	▪ solvents ▪ waste oils ▪ waste plastics
Material content (CaO, Fe_2O_3, Al_2O_3 etc.) → Material recycling Energy content (carbon, hydrogen) → Energy recovery	▪ substitution of raw material ▪ substitution of fossil energy	▪ used tires ▪ used paints ▪ industrial sludge
Material content (CaO, Fe_2O_3, Al_2O_3 etc.) → Material recycling	▪ substitution of raw material	▪ molding sand ▪ blast furnace slag ▪ fly ash and bottom ash ▪ by product gypsum

Co-processing of Organic Hazardous Waste in Cement Kilns

- …is accepted to be a suitable treatment option in current European, US and other regulations but needs to comply with ELV's and other performance requirements.
- Almost 40 years of experience around the world have shown that emissions from facilities co-processing hazardous waste as a substitute fuel are not significantly different from those burning conventional fuel.
- More than 10 million tons of Hazardous Wastes are co-processed in cement kilns world-wide annually.

Firing a cement kiln means feeding continuous streams of uniform quality combustible materials

- The example of mineral coal as the generic case for all (natural and alternative) fuels:



Arrow = transport processes
1 = Storage of raw coal
2 = Fine coal silo
3 = Kiln system

Desired characteristics of cement kiln fuels:

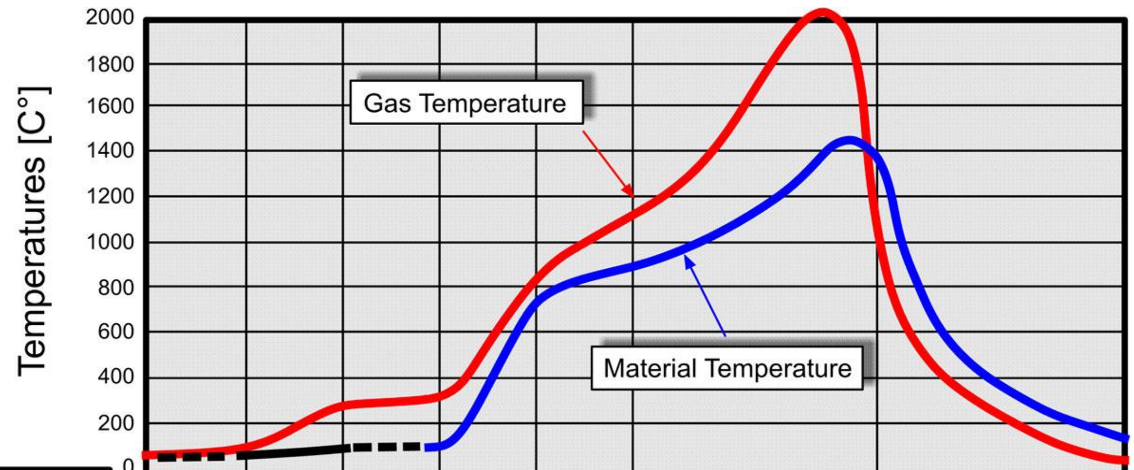
- Continuous availability in large quantities
- High and uniform quality
  - Low water/low ash/fineness appropriate for feed point
  - Good flowability/metrability for low excess air combustion
- Not inducing environmental damage

Summary of special features in cement kilns

1. High to very high system temperatures.
2. Process Inherent multi-stage fluidized bed gas cleaning technology.
3. Huge Retention capacity for SO_2 and Cl.
4. Atmospheric emissions largely given by roasting off of volatile raw material components.
5. All mineral Input turned into product.
6. All trace elements (heavy metals) safely embedded in final product.
7. High thermal efficiency of process.
8. Reduction of country CO_2 emissions through alternative fuels utilization.

No. 1: High to very high system temperatures

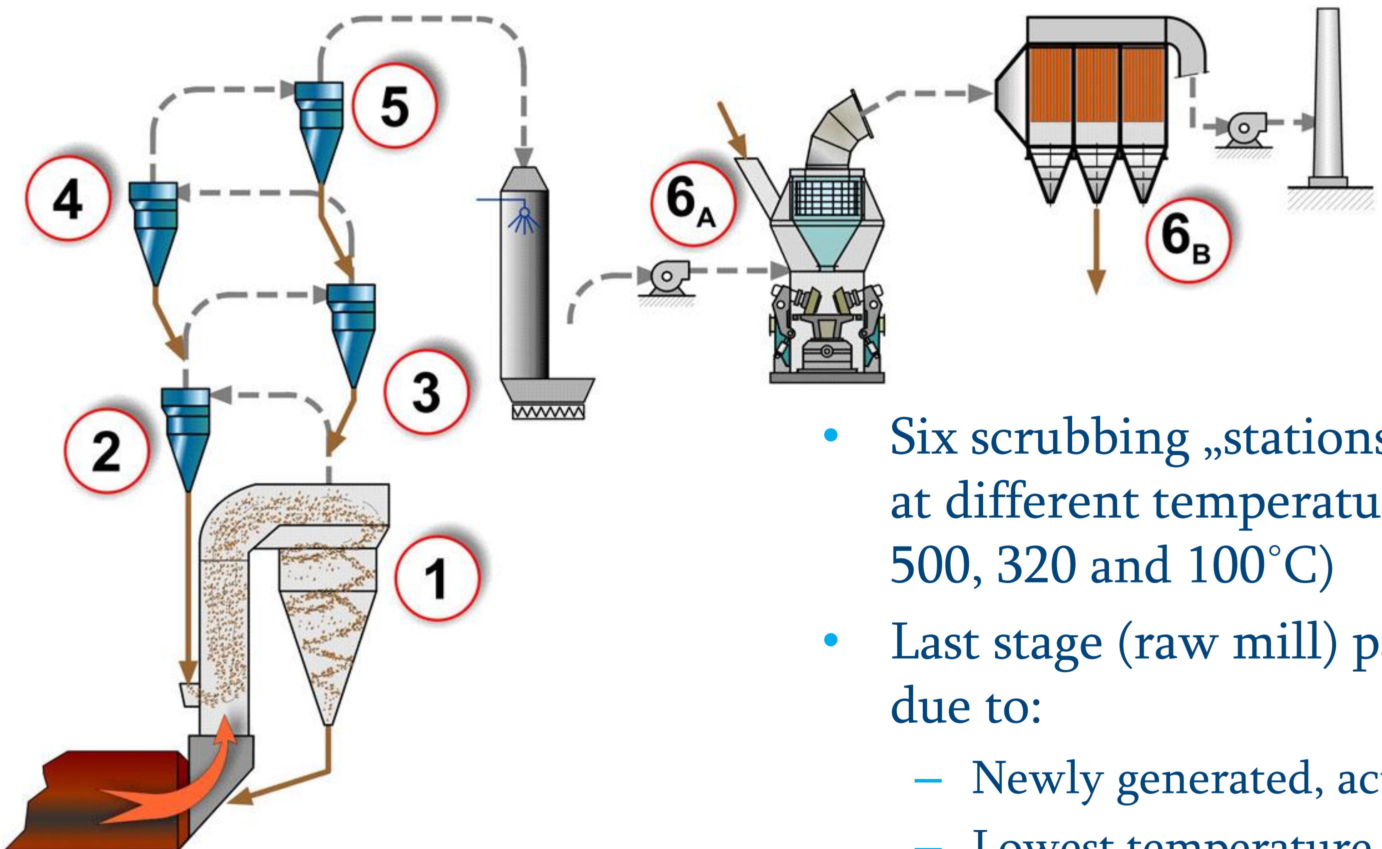
- Result in complete combustion down to traces of CO in the rotary kiln: all organic input is reliably destroyed (oxidized)



Equipment	Filter	Raw Mill	Gas duct and cooling tower	Preheater	Precalciner	Rotary Kiln	Cooler
Gas retention time	ca. 15s	ca. 2s	ca. 10s	ca. 10s	ca. 3s	ca. 10s	ca. 1s
Material retention time	60s - 30min.	30s - 30min.		ca. 50s	ca. 5s	ca. 30min	ca. 30min

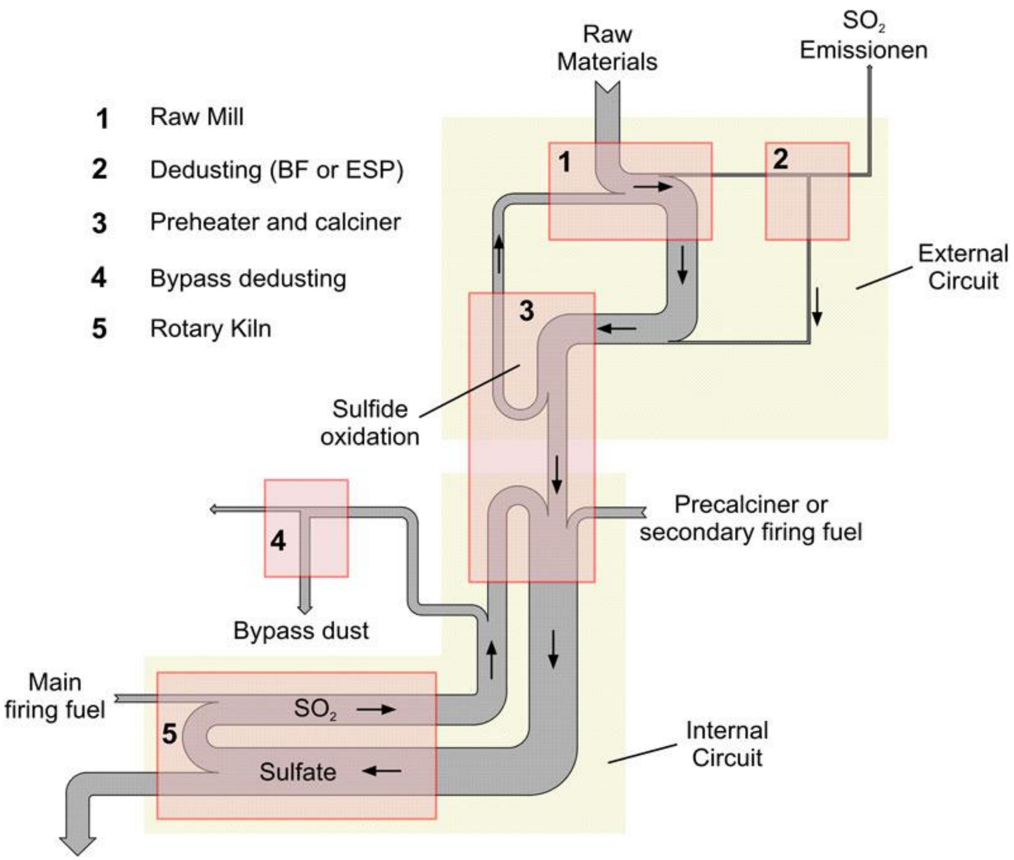
Note: Even the most stable organic compound cannot survive temperatures exceeding slightly more than 800 °C

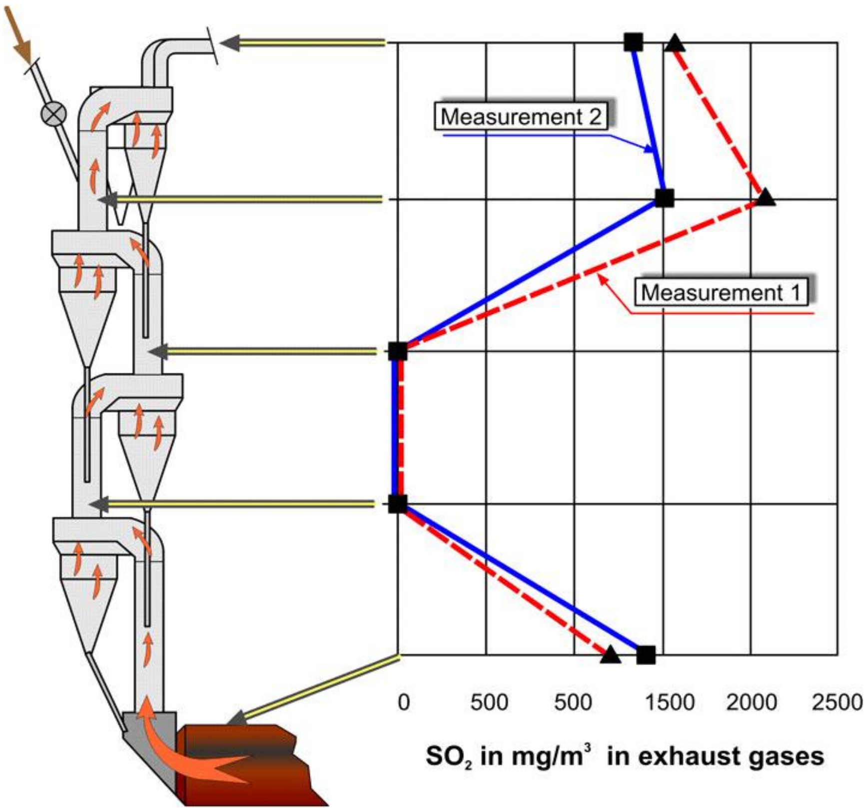
No. 2: Process inherent multi-stage fluidized bed gas cleaning technology



- Six scrubbing „stations" in series, working at different temperatures (850, 750, 650, 500, 320 and 100°C)
- Last stage (raw mill) particularly effective due to:
  - Newly generated, active surface
  - Lowest temperature
  - Highly efficient bag filter (>10 mg/Nm^3 clean gas dust)

No. 3: Huge retention capacity for SO_2 and Cl





No. 4: Atmospheric emissions largely given by roasting off of volatile raw material components

Emission component of importance in the cement industry	Range of emissions found [mg/Nm^3]	European ELV acc. to WID [mg/Nm^3]	Origin of emissions
SO_2	0 – 300 - 3000	50 plus	Pyritic S in raw materials
NOx	300 - 2000	200?/500/800	Main flame in rotary kiln + fuel NO
VOC	0- 50 - 500	10 plus	Organics in raw materials
HCl	1 – 15	10	Raw materials and fuels
NH_3	1 – 15 – 40	None	Raw materials and possible SNCR
Benzene (C_6H_6)	1 -2 - ….	5	Organics in raw materials
PCDD/DF	0 – 0.02 ng ITE	0.1	Organics in raw materials
Hg	0 - 1	0.05	Raw materials and fuels
Tl and Cd	traces	0.05	Raw materials
Other 9 heavy met.	Σ< 0.5	0.5	Raw materials
Clean gas dust	1 – 20 – 50 - 150	30	Raw materials

No. 5: All mineral input turned into product

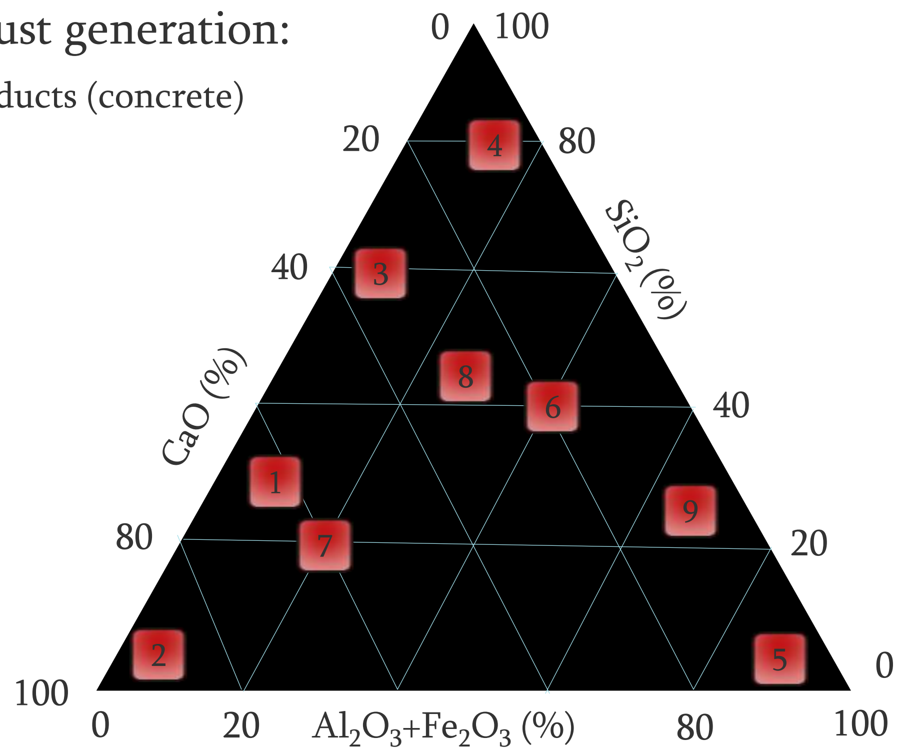
- All main and minor elements (particularly also those imported with alternative materials) are used to form clinker minerals or are incorporated in clinker minerals

Exeptions in case of bypass dust generation:

- Incorporation in hydration products (concrete)
- Landfilling

Legend

1. Clinker
2. Limestone
3. Marl
4. Foundry sand
5. Pyrite ash
6. Coal ash
7. Lignite ash
8. Sewage sludge ash
9. Tire ash



No. 6: All trace elements (heavy metals) safely embedded in final product (I)

- All heavy metals (HM) are
  - incorporated in the clinker minerals (exept Hg and Tl)
  - bound in hydration products (also Tl and much of Hg)
  - encapsulated in the concrete structures

Concrete is a multi-barrier system preventing migration (leaching) of heavy metals to the living environment

Leaching tests	Test results
Monolithic concretes, all leaching test methods	All HM below or close to detection limit even of most sensitive leaching test method
Crushed concrete, most agressive test method	Leached concentrations of chromium, aluminium and barium may come close to drinking water standards. Conclusion: limit chromium input to the minimum

No. 6: All trace elements (heavy metals) safely embedded in final product (II)

- To prevent abuse (of concrete as a final storage facility for HMs), do not exceed e.g. the following HM concentrations in alternative fuels (AF) (mg/kg)

Tl	Cd	Be	Cr	As	Sb	Sn	Co	Pb	Ni	Cu	V	Hg
50	50	50	250	400	500	500	500	800	1000	1000	1000	5

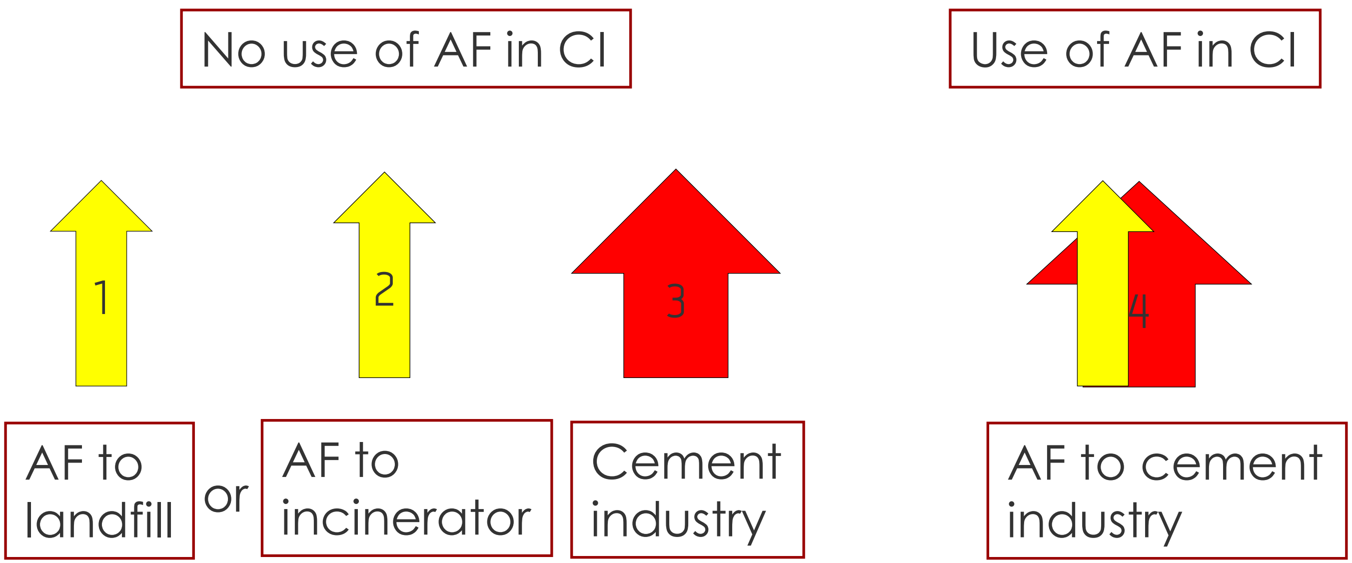
No. 7: High thermal efficiency of process

- Specific heat consumption of process: 3000 – 3300 kJ/kg cli
- Theoretical heat demand of clinker formation: 1750 kJ/kg cli
- Thus, thermal efficiency: 53 – 58 %
- Thermal efficiency at maximum waste heat utilization (kiln exhaust gas and cooler exhaust air: 80 -90 %

- Example of a kiln system heat balance (orders of magnitude only):
  - Clinker formation 1750
  - Exhaust gas heat content 700
  - Exhaust air heat content 400
  - Radiation and convection losses 250
  - Clinker heat content 100

Total: 3200 kJ/kg of clinker

No. 8: Reduction of country CO_2 emissions through alternative fuels (AF) utilization



1. Landfill gas (CO_2 and CH_4)
2. CO_2 from incineration
3. CO_2 from fossil fuels in CI
4. CO_2 from both systems if AF used in CI

Other options for CO_2 reduction:

- Reduction of cli/cem factor
- Process improvements (including waste heat utilization)

Five main types of waste used as alternative fuels (and the ash as AR)

Fuel Main Types (families)	Characteristics	Examples
Liquid AFs	Can be atomized with compressed air (solid particles in liquid <2-4mm), all feed points possible	Spent solvants, waste oils, emulsions, waste water, depleted pesticides
Sludges	Pumpable with piston pumps, then to be handled identically to lump fuels	Paint sludges, petroleum/oil sludges
Lump fuels	Heavy material, cannot be carried by kiln gases; is fed to, gasified and burnt at kiln inlet	Whole waste tires, toner cartridges, filter cakes
Coarse solids: < 50 mm solids (3-dimensional) and < 200mm foils (2-dimensional)	Can be carried vertically by kiln gases (thus suitable for precalciner)	Tire chips, coarse shredded plastics and textiles, shredded waste wood
Fine solids: < 5 mm solids (3-dimensional) and < 50mm foils (2-dimensional)	Can be transported pneumatically and carried horizontally by kiln gases (suitable for main firing)	Impregnated saw dust, animal meal, dried sewage sludge, finely shredded plastics and waste wood

Materials commonly not used in a cement kiln

Banned wastes	Undesired HM in clinker	Emission values	Occupat. health and safety	Preferable recycling options	Impacts on kiln operation
Electronic waste	x	x		x	
Whole batteries	x	x		x	x
Bio-active medical waste			x		
Mineral acids and corrosives		x	x		x
Explosives	x		x		x
Asbestos			x	(landfills)	
Radioactive waste	x		x		
Unsorted garbage	x	x		x	x

HM= heavy metals

General principles for input control

1. Many regulations do not restrict the use of AFRs to certain categories or concentration limits, they rely on emissions limits only (most common).

2. Some regulations specify an explicit list of acceptable AFRs with maximum and/or minimum values for various parameters, e.g. heavy metals, chlorine, calorific value etc. called the "positive" list (plus # 1).

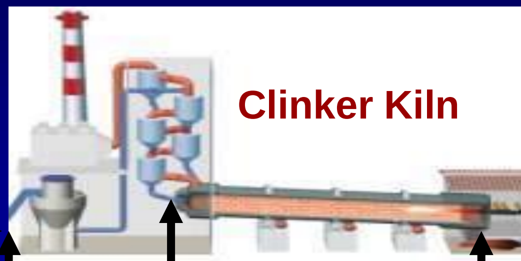
3. Some specify an explicit negative list of waste categories which are not allowed used (plus # 1).

4. Some require performance verification, or test burn, in addition to # 1.

Wastes co-processed in the cement industry

✶ **Clinker Production**

Raw Material



Clinker

✸ **Cement Production**

Cement Mill

Cement

AFR	AFR	MIC
Only Raw Material	**Raw material and fuel**	**Only Raw Material**

Examples of AFR used primarily as alternative raw material:

Aluminum hydroxide residues, catalysts, foundry sands, SPL refractory fraction etc.

Examples of AFR used in the kiln for the production of clinker primarily as alternative energy source:

Solvents, paint residues, hyrdocarbon residues, wood, paper, sludges from industrial waste water treatment, SPL carbon, soils/plastics/textiles contaminated with hydrocarbons, pesticides, etc.

Examples of MIC (mineral components) that are added to the clinker for the production of cement:

Ground slag (steel), fly ash (power plants), alternative gypsum sources, etc.

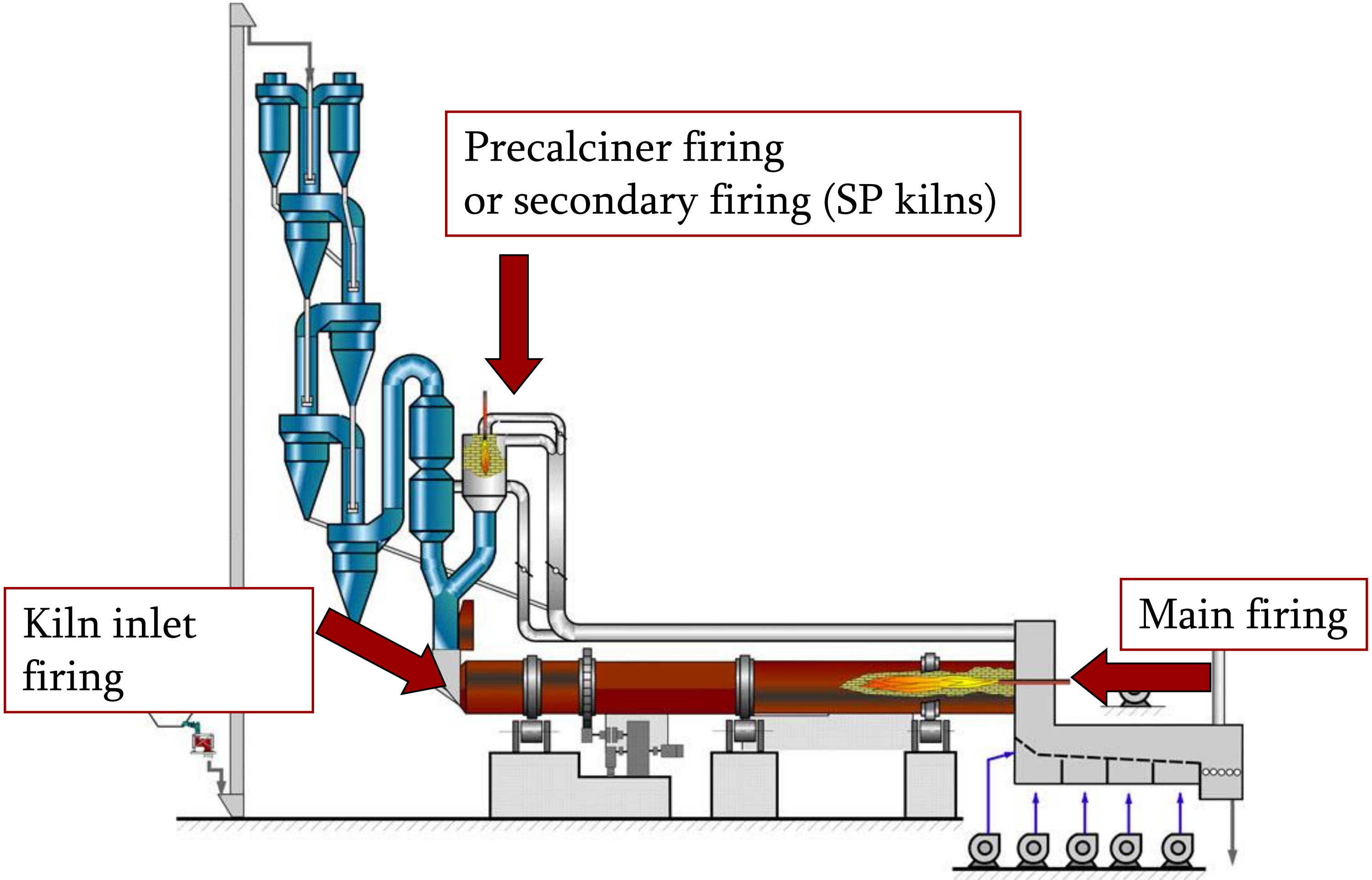
Alternative fuels are sources of energy and raw materials (I)

Fuel type	Net Calorific Value [MJ/kg]
Polyethylene	46
Light fuel oil / Diesel (for comparison)	*42*
Heavy fuel oil (for comparison)	*40*
Tar	38
Animal fat	37
Rubber	36
Waste oils, refinery wastes	30 to 40
Petcoke (for comparison)	33
Waste tires	28 to 32

Alternative fuels are sources of energy and raw materials (II)

Fuel type	**Net Calorific Value [MJ/kg]**
Bituminous coal (low ash) for comparison	*27*
Combustible substitution liquid	20 to 30
Plastic fluff	18 to 22
Landfill gas	16 to 20 (per Nm^3)
Animal meal	18
Dry wood, rice husks (10% H2O)	16
Impregnated saw dust (25% H2O, CSS, Seneffe)	10 to 13
Dried sewage sludge (10% H2O)	10
Unsorted domestic refuse (30% H2O)	8.5

Fuel feed point in cement kiln systems



Do not overload the feed points

Feed point	Liquid AF	Fine solid AF	Coarse solid AF	Lump AF
Main firing	up to 100	up to 30	-	-
Kiln inlet firing and secondary firing	up to 15	up to 15	up to 15	up to 15
Precalciner firing	up to 60	up to 60	up to 60	-

All numbers in % of total fuel energy input; Numbers are orders of magnitude (optimization by testing)

Pre-treatment of wastes

All materials (in the form of AFRs) introduced into a cement production process should ideally resemble the homogeneity, particle size distribution, heat and water content and chemical composition as normal fine coal and raw meal used in cement manufacturing.

As waste materials often are heterogeneous, pre-treatment and pre-processing are often necessary.

Measuring emissions from a cement kiln

- Continuously measured emission components
  - Always, mandatory: Dust, SO2, NOx (NO), VOC
  - Sometimes, but possible: NH3, HCl, HF, Hg, benzene etc.
- Discontinuously measured emission components
  - Always mandatory: NH3, HCl, benzene, PCDD/DF, 12 heavy metals (including Hg, Tl, Cd, …)
- Regular measuring campaigns according to permits.

- Baseline emission measurements as well as trial burn emission measurements use this same approach

Avoiding additional emissions

- Select the appropriate feed point(s)
- Do not overload the feedpoints
- Assure always complete combustion conditions in the kiln
- Allow no or very low, and uncritical organics in alternative raw materials only (specially watch PCDD/DFs and keep them away)
- Watch the mercury and keep it away
- (Watch the chromium and keep it away whenever possible)
- Extract direct operation filter dust and feed it to the cement mill
- Watch volatile sulfur in AR and keep it away or abate it, if required

What may happen if rules are not adequately observed

Basic Rule	Effect of Basic Rule Violation
Basic prerequisits deficient	Authority , NGO and neighbour relations at stake
Wrong feed points	VOC and CO emissions may increase, product quality problems to be expected
Feed points overloaded	Same as above
Reducing kiln atmosphere	Same as above plus operational problems
High organics content of raw materials (presence of D/F precursors)	Same as above. D/F emissions may increase at low levels
Excessive Hg in raw materials	Hg emissions increase
Excessive volatile sulfur in raw mats.	SO_2 emissions increase
Use of extremely low grade fuels (high water, high ash, high chlorine, coarse, quality and quantity fluctuations, cold air intakes)	Increase of specific heat consumption Possibly more greenhouse gases Possibly requirement for by-pass system

Emission abatement techniques

Emission	Available abatement methods
Stack dust	Well maintained bag filters or electrostatic precipitators
SO_2	Hydrated lime injection to top riser duct (max.1200 → 500) Wet sulfur scrubber (for large emissions, up to 3000 → < 200)
NOx	SNCR with NH_3 injection
VOCs	Nothing really satisfactory (activated carbon absorbers, catalytic converters , thermal oxidisers)
HCl	Indirectly via kiln and DOM dust bypass to RM
NH_3	Indirectly via DOM dust bypass to RM
C_6H_6	Nothing reasonable for the time being
PCDD/DF	No emission problems. In the rare case of elevated emissions: Indirectly via DOM dust bypass to RM and reduction of precursors
Hg/Tl	Input control and limitation, indirectly via DOM dust to RM
Other HM	No emission problems

DOM = Direct Operation Mode of kiln/raw mill system (RM)

Benefits of co-processing AFRs and treatment of organic hazardous wastes in cement kilns

- Facilities and infrastructure are already in place;
- Recovers energy & conserves fossil fuel & raw materials;
- Inherent features, e.g. time & temperatures, are excellent for organic hazardous waste destruction;
- Usually no residues to dispose of;
- Emissions will normally be unaffected if properly operated;
- Reduces disposal costs and CO2 emissions compared to landfilling and incineration.

Successful implementation of co-processing

A number of conditions should ideally be in place prior to commence on large scale co-processing activities, e.g. co-processing acceptance, availability of sufficient waste materials with adequate quality, polluter-pays-principle, long term predictability and the right climate for investments, a level playing field, technical and environmental competence, a robust regulatory framework and permitting conditions.

Cement manufacturers are vulnerable

Co-processing is still controversial among some stakeholders and one accident may under worst case conditions undermine co-processing acceptance in the entire industry, i.e. all players have the responsibility to minimize risks and strive towards excellence and best practice to protect the reputation.

Summary of recommendations and best practice for co-processing

- An approved EIA and all necessary national/local licenses.
- Compliance with all relevant national and local regulations.
- Compliance with the Basel and the Stockholm Convention.
- An approved location, technical infrastructure and processing equipment.
- Reliable and adequate power and water supply.

Summary of recommendations and best practice for co-processing

- Adequate air pollution control devices and continuous emission monitoring ensuring compliance with regulation and permits - needs to be verified through regular baseline monitoring and reporting.
- Rapid exit gas conditioning/cooling and low temperatures (<200^0C) in the air pollution control device to prevent dioxin formation.
- Clear management and organizational structure with unambiguous responsibilities, reporting lines and feedback mechanism.

Summary of recommendations and best practice for co-processing

- An error reporting system for employees.
- Qualified and skilled employees to manage wastes and health, safety and environmental issues.
- Adequate emergency and safety equipment and procedures, and regular training.
- Authorized and licensed collection, transport and handling of wastes.
- Safe and sound receiving, storage, preparation and feeding of wastes.

Summary of recommendations and best practice for co-processing

- Adequate laboratory facilities and equipment for waste acceptance and feeding control.
- Demonstration of wastes destruction performance through test burns.
- Adequate record keeping of wastes and emissions.
- Adequate product quality control routines.

Summary of recommendations and best practice for co-processing

- An environmental management and continuous improvement system certified according to ISO 14001, EMAS or similar.
- Regular independent audits on all aspects of co-processing and independent emission monitoring and reporting.
- Regular stakeholder dialogues with local community and authorities, and for responding to comments and complaints.
- Open disclosure of performance reports on a regular basis.