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SUMMARY

This article is the second part of the series of excerpts from the "Alternative Fuels and Raw Materials Handbook for the Cement and Lime Industry." In the first part, the author presented the environmental laws and emission limits including the latest developments. In this context, Dirk Lechtenberg emphasized the difficulties involved in the use of alternative fuels. To meet the increasingly stringent emission limits in the long run, the material composition of the fuels should vary only slightly. The high quality of alternative fuels is thus the basis for a permanently successful substitution of fossil fuels. Therefore, this article focuses on quality management and quality assurance.

ZUSAMMENFASSUNG

Dieser Artikel ist der zweite Teil aus der Serie von Auszügen aus dem „Alternative Fuels and Raw Materials Handbook for the Cement & Lime Industry". Im ersten Teil stellte der Autor aktuelle Umweltgesetze und Emissionsgrenzwerte vor und wies in diesem Zusammenhang auf Problematiken hin, die der Einsatz alternativer Brennstoffe mit sich bringt. Um die immer strenger werdenden Emissionsgrenzen langfristig einhalten zu können, ist u. a. die Qualität der alternativen Brenn- bzw. Rohstoffe von entscheidender Bedeutung. Hohe Qualität der alternativen Brennstoffe ist folglich die Basis für eine dauerhaft erfolgreiche Substitution fossiler Brennstoffe. Dieser Beitrag wendet sich daher nun der Qualitätssicherung und dem Qualitätsmanagement im Detail zu.

(English text supplied by the author)

Quality management of alternative fuels

Qualitätsmangement von alternativen Brennstoffen

1 Introduction

Quality assurance is the foundation for the processing of suitable waste materials and biomass into environmentally compatible and cost-saving substitutes for fossil fuels. As is the case in the clinker production process, knowledge of the waste and raw materials at hand is the first step towards the production of an even quality product.

In general, ashes from alternative fuels are bound in the clinker. This is of particular importance since many waste products contain contaminants which can have a harmful influence on the cement/lime as well as a negative effect on emissions. Furthermore, alternative fuels frequently contain volatile elements (chloride, alkalis, sulphur) which increase the internal salt cycle and can lead to build-up problems in the kiln and heat exchanger. In order to avoid negative impacts resulting from both contaminants and volatile elements, continuous sampling and knowledge of the wastes and raw materials are vital.

The quality management system for alternative fuels from waste is divided into two areas:

a) Quality management in the RDF production plant
b) Quality management (control) system in the cement/lime plant

Both quality assurance systems should be matched to each other. Also, on the one hand, it is necessary to adhere to the legal parameters for employment of alternative fuels in cement/lime plants and on the other hand to follow the production-specific parameters.

2 Environmentally relevant elements

Belonging to the environmentally relevant elements are those listed in e.g. the Directive 2000/76/EC of the European Parliament and of the Council [1]. This list is not exhaustive, from time to time further elements can be requested by the authorities. In most cases these elements are heavy metals such as cadmium, thallium, mercury, lead, chrome, cobalt, copper, manganese, nickel and vanadium. In general, metals with a density of more than 5 g/cm^3 are designated heavy metals [2]. These elements and their compounds naturally only occur in traces. A few of these heavy metals are vital for living organisms, for example, copper, manganese, vanadium, iron, and zinc [3]. They are designated as biologically essential metals or trace elements. Further heavy metals, the non-essential trace elements, like mercury, thallium or lead are not needed by living organisms. In slightly increased concentrations, essential as well as non-essential heavy metals can induce serious damage to health in humans and many other living organisms. The toxic effect of a particular heavy metal depends decisively on the respective chemical form. Trivalent chrome is valued at pH 7 as a non-soluble hydroxide and can only be absorbed by an organism in traces. Hexavalent chrome however is very soluble as chromate ($CrO4^{2-}$) and can be very well absorbed by an organism. Special attention should be paid here, since chromate is suspected of having a carcinogenic effect [3].

Also arsenic and antimony, often even selenium and tellurium are among the environmentally relevant elements. The entire group of environmentally relevant elements is often designated as "heavy metals", which is not correct. Arsenic, antimony and tellurium are categorised as semimetals – depending on the occurring modification these elements have metallic or nonmetallic characteristics [2]. Selenium is even considered a non-metal [2].

3 Contaminant sources in alternative fuels

In order to minimise the introduction of contaminants, especially environmentally relevant elements (mainly heavy metals) into alternative fuels, the people in charge in the cement and lime industry need to be schooled and trained on a continual basis. Fundamental knowledge of possible contaminant introduction through waste-sourced fuels or through biomass products must be transmitted.

Environmentally relevant elements reach waste via various old products. The metal content in household waste and in similar mixed wastes is a major cause though not the only one. Investigations illustrate [4, 5] that the highest concentrations of certain heavy metals mainly occur in fractions of electronic scrap, fine fractions, batteries, metals, some plastic objects, composites and leather. The latter has high chrome contents which derive from leather tanning by chromate salts.

In the following, environmentally relevant elements are listed as examples with sample applications, general details on the physiognomic efficiency and their relevance in the biosphere.

Figure 1: Fully automatic sampling at RDF unloading station; Photo: MVW Lechtenberg

PROCESSING

Figure 2: Sampling utilising a sampling vessel; Photo: MVW Lechtenberg

Antimony, Sb

- Fireproofing agent (antimony trioxide) in
  - o plastics
  - o electronic devices
  - o mattresses
  - o insulating material for motor vehicles (roof-linings, door panel trim, carpets)
  - o technical foams
  - o curtains, furniture covering materials (in many countries, e.g. England, also home textiles must be finished with flame-retardants for legal fire-protection reasons)
- Additives for pigmentation in PET-plastics
- Alloy additive for hardening of metals in semi-conductor technology
- Alloy component in lead lettering in the printing industry (also zinc and copper)
- In lead batteries (improvement of flow behaviour, creep resistance, fatigue strength and electrochemical stability)
- Sb oxides: Colour pigments for ceramics, glasses, plastic
- Promoter in polyester production, production of pesticides, pickling and fireworks articles

Arsenic, As

- Alloy constituent of Cu, Sn and Pb in metals
- In electronic components (semi-conductors)
- As residual waste in treated wood (arsenic salts)
- In rat poison, pesticides and wood protection agents, e.g. copper-arsenite-acetate for pest control in wine-growing
- In medicine, e.g. in medication for cancer therapy

Arsenic oxide As_2O_3 is a strong poison and a carcinogen for humans even in very small amounts.

Cadmium, Cd

- Nickel-cadmium and silver-cadmium batteries
- Pigments and stabilisers (cadmium sulphide in yellow plastics, especially PVC)
- Electrolytic rust protection
- Electrode material

Cadmium and its compounds are categorised as toxic.

Chrome, Cr

- Alloy component in stainless steel: min. 10.5 % chrome
- As galvanic coatings
- In small metal items (fashion jewellery, jeans buttons)
- Chrome bearing pigments and tanning salts (leather)
- Green colouring of glasses and porcelain (with Cr_2O_3)
- Yellow pigment lead chromate ($PbCrO_4$) (once used as paint but owing to its toxicity nowadays hardly of any significance)
- CrO_2 is a magnetic strip component

Chrome is frequently present in mixed building site waste caused through friction during processing/comminution of chrome metallic parts – especially in fine fractions. Above all, hexavalent chromate (CrO_4^{2-}) which can trigger carcinoma ("bricklayer's itch"/"mason's itch") needs to be mentioned here within the sphere of harm to human health.

Cobalt, Co

- Potassium cobalt silicate for colouring of glasses (cobalt blue, cobalt glass) and ceramics
- Alloy component for the production of corrosion resistant alloys
- Alloys for permanent magnets
- Alloys of cobalt, chrome and tungsten are very hard and are used for tools (chisel tips)
- Component of "WiDia" (sinter material of tungsten carbide and 10 % cobalt, employed in the production of cutting tools, e.g. drills)
- Promoter in chemical synthesis (e.g. hydroformylation, desulphurisation)
- In Li-Co batteries
- Additive in fertiliser and feed agents in cobalt-poor ground
- Production of paints (as colouring component, as drying agent)

Cobalt plays a significant role in biochemistry. In Vitamin B_{12} Co forms the central atom.

Copper, Cu

- Conducting material in electric technology (coils for electrical motors, spools, generators, transformers, cables and switchgear; live conductors in high, medium and low voltage und networks and electronics (wiring in semi-conductor chips))
- Building field: Roof, gutter and facade material
- Pipes and fittings for drinking water supply and heating installations
- Small items such as office clips, document bindings
- Copper-zinc-alloys (= brass): Handles and door furniture, decorating material
- Copper-tin-alloys (= bronze): Decorating material
- Coin metal ("German silver" or "nickel silver" = Cu-Ni alloy)
- Copper salts as fungicide in plant protection and in wood protection agents
- Copper-sulphate solutions for galvanising
- In the medical field:
  - o As disinfection agent
  - o In homeopathic ointments
  - o In contraception

Copper is an essential trace element constituent of many enzymes.

Lead, Pb

- In batteries
- Lead metal foils for roof sealings
- As alloy component in bottle capsules, tubes and tinsel (stanniol = tinned lead foil)

Table 1: Proposal for the characterisation of alternative fuels (Source: MVW)

Material Composition	Value	Unit
Moisture		Ma.-% ar
Ash		Ma.-% d
Biodegradable ingredients		Ma.-% d
Short Analysis		
Fixed carbon		Ma.-% daf
Volatiles		Ma.-% daf
Elemental Analysis		
C		Ma.-% daf
H		Ma.-% daf
O		Ma.-% daf
N		Ma.-% daf
S		Ma.-% daf
Cl		Ma.-% daf
F		Ma.-% daf
Mechanical Characteristics		
Bulk density		kg/m^3 ar
Grain-size distribution		Ma.-%
Caloric Characteristics		
Gross calorific value		MJ/kg daf
Net calorific value		MJ/kg daf
Reaction Engineering Characteristics		
Ignition and combustion behaviour		

Trace Analysis	Value	Unit
As		mg/kg d
Be		mg/kg d
Cd		mg/kg d
Co		mg/kg d
Cr		mg/kg d
Cu		mg/kg d
Hg		mg/kg d
Mn		mg/kg d
Ni		mg/kg d
Pb		mg/kg d
Sb		mg/kg d
Se		mg/kg d
Sn		mg/kg d
Te		mg/kg d
Tl		mg/kg d
V		mg/kg d
Ash Composition/Ash Melting		
Al		mg/kg d
Ca		mg/kg d
Fe		mg/kg d
K		mg/kg d
Mg		mg/kg d
Na		mg/kg d
P		mg/kg d
Si		mg/kg d
Ti		mg/kg d
S (min) or sulfate content		mg/kg d
Softening temperature		°C
Hemisphere temperature		°C
Flow temperature		°C

Abbreviations:
ar = as received
d = dry
daf = dry and ash-free

- Soldering
- In tin soldiers
- Lead strips for curtain weighting

Figure 3: Sample preparation table; Photo: MVW Lechtenberg

- Lead in glass (monitor tubes, lead crystal)
- As stabiliser (PVC-cable sheathing)
- Colour and corrosion protection pigments (Pb_3O_4)
- For protection against radioactive beams (e.g. lead aprons in nuclear medicine)

Tetraethyl lead was in petrol as an anti-knocking agent component. Lead and lead compounds, in particular the organic lead compounds, are categorised as toxic.

Manganese, Mn

- Alloy constituent for iron (manganese steel) and other metals
- In dry batteries (as MnO_2 in coal-zinc batteries)
- In the production of ceramics
- Potassium permanganese production (strong oxidising agent)
- Manganese sulphate for enrichment of manganese-poor soils
- Manganese oxide (MnO_2) to decolour green, iron containing glass

Table 2: Example of a specification for waste-derived alternative fuels (Source: MVW)

Quality guidelines for suppliers of secondary fuels **Specification of combustibles from industry and trade wastes** **Textile, paper, rubber, plastic and composite plastic fractions** Composition according to Waste Key Numbers, see form "Declaration Analysis"			
Designation of the material	**Composition**		
	Com-ponents	**Proportion mass % practice value**	**Maximum value**
Mechanical characteristics: – Maximum particle size < 15 mm One dimensional (films two dimensional) – Hard plastic proportion ≤ 0 % – Dust content < 0.5 mm, max. 10 %			
Calorific value, as received:	NCV, ar	20 to 24 MJ/kg **(min. 20 000 kJ/kg)**	
Moisture:	H_2O	12	20
	H		
	S		1
	O		
	N		5
	C		
	Cl^-	0.5	
	F^-		0.05
Ash content:	Ash		25
		Practice value prop. [mg/kg]	Max. value prop. [mg/kg]
Trace elements related to DS:	Cd	3	5
	Tl	1	2
	Hg	0.6	1
	Sb	25*)	60*)
	As	9	20
	Pb	50	100
	Cr	40	120
	Co	8	15
	Cu	100	150
	Mn	50	150
	Ni	50	100
	V	10	20
	Sn	20	50
	Be	0.4	2
	Se	5	10
	Te	5	20
	Zn		2 000
	PCB	Sum acc.to DINx5	3

*) independent of analysis process

Manganese is an essential trace element constituent of many enzymes (e.g. peroxidases).

Mercury, Hg

In batteries: Alkali-manganese, mercury oxide-batteries
In the medical field:
- o Amalgam from dental practices
- o Formerly used in pharmaceuticals as antiseptic (calomel Hg_2Cl_2) or as a disinfection agent (sublimate $HgCl_2$)

Measuring instruments (barometer, hygrometer, thermometer)
Fluorescent lamps (mercury vapour lamp)
Colour pigments (cinnabar)
Electric mercury switches
In agriculture as fungicide and bactericide
Electrolytic preparation of chlorine
In diffusion pumps for high vacuum
Gold extraction (amalgam formation between gold and mercury)

Owing to its toxicity the use of mercury was generally in decline. However, through the use of energy-saving light bulbs this development has been reversed: The proportion of mercury in household waste as well as in mixed industrial and trade waste has increased significantly over the last few years. Thanks to the long lifespan of energy-saving lamps a further increase is anticipated in the coming years leading to significant changes in the composition of refuse-derived fuels for the cement industry due to the fact that sources originated from municipal solid wastes which may contain damaged light bulbs have to be exempted from the list of suitable wastes for co-processing.

Nickel, Ni

In steel refining
Stainless steel: ≥ 2.5% nickel
In domestic waste in metal fractions (Ni-Cd batteries)
In fashion jewellery and coins
Fine nickel parts serve as a technical hydrating accelerator, e.g. in the hardening of fat.

Nickel is a trigger for skin allergies. In the biosphere nickel plays a role as an essential trace element in various enzymes of bacteria and plants (e.g. urease).

Thallium, Tl

In the production of special glasses (infra-red transmissive glasses, low melting-point glasses)
In semi-conductor technology (e.g. thallium sulphide in photo cells)
Thallium(I)sulphate as rat poison

Thallium and thallium bearing compounds are highly poisonous.

Vanadium, V

Improvement of steel wear resistance
Vanadium pentoxide as catalyst in sulphuric acid production

In the biosphere vanadium occurs as a constituent of various enzymes in bacteria (e.g. nitrogenase).

Zinc, Zn

Galvanising of steel for corrosion protection
Brass products
Semi-fabricates in the form of
- o Steel plate (pre-weathered titanium zinc for the areas of roofing, facades and roof drainage)
- o Wires (thermal spray wires)
- o Strips (blow-out fuses)
- o Anode (dry batteries)

Alloys in cast zinc

Table 3: Example of a template for a declaration analysis (part I): Composition of waste-derived alternative fuels (Source: MVW)

Declaration analysis for RDF – waste composition			
Composition [%]	**EWC-Number**	**EWC-designation**[1), 2), 3)]	**Exemplary explanation**
	02 01 04	Waste plastics (except packaging)	PUR-foam, PE compounds
	03 03 07	Mechanically separated rejects from pulping of waste paper and cardboard	
	03 03 08	Wastes from sorting of paper and cardboard destined for recycling	Inappropriate paper qualities, other high-caloric ingredients
	04 02 09	Wastes from composite materials (impregnated textile, elastomer, plastomer)	Textiles, carpets, fleeces and insulation materials from the car interior, hygiene products (both raw material from scrap)
	04 02 21	Wastes from unprocessed textile fibres	Raw material, scrap, etc. from the textile industry
	04 02 22	Wastes from processed textile fibres	Carpet remnants, car textile (both raw material and scrap, edge sections)
	07 02 13	Waste plastic	Plastic and rubber waste
	08 01 12	Waste paint and varnish other than those mentioned in 08 01 11	Only hardened paints and varnishes
	08 02 01	Waste coating powders	
	09 01 07	Photographic film and paper containing silver or silver compounds	
	09 01 08	Photographic film and paper not containing silver or silver compounds	
	12 01 05	Plastic and turnings	Automotive plastics, PU composites, injection moulded components, foams
	15 01 01	Paper and cardboard packaging	Decoration paper, packaging and label paper (residues from the production), also wax impregnated paper
	15 01 02	Plastic packaging	Packaging films (raw material and scrap), foams, polystyrene
	15 01 05	Composite packaging	Plastic and paper laminates
	15 01 06	Mixed packaging	Packaging of the group no. 15 01
	15 02 03	Absorbents, filter materials, wiping cloths and protective clothing other than those mentioned in 15 02 02	Absorbents, filter materials, wiping cloths, protective clothing
	16 01 03	End-of-life tyres	End-of-life tyres, shredded tyres
	17 02 03	Plastic	
	19 05 01	Non-composted fraction of municipal and similar wastes	
	19 12 01	Paper and cardboard	
	19 12 04	Plastic and rubber	
	19 12 08	Textiles	
	19 12 10	Combustible waste (refuse derived fuel) max 10 % of the total mix	High calorific valuable fractions of the mech. or mech. biolog. treatment of waste (90 to 95 % of combustibles are known from the positive list and/or the waste groups 20 02 and/or EWC 17 09 04)
	Sum in % (without 19 12 10)		

Notes/comments

1) additional types of waste in compliance with the practical and maximum values!

2) without fine particle fraction! Proportion of grain size ≤0.5mm max. 10%!

3) only dehydrated, maximum moisture content according to quality specifications

Additives in various industrial areas (zinc oxide, zinc powder and zinc dust)

As stabiliser for plastics

Zinc sulphates in the textile and synthetic fibre industry

Paints and lacquers: Active pigment to control certain lacquer characteristics such as through-drying, fungal resistance and weather resistance

Zinc oxide: Production of glues based on natural and synthetic rubber

Zinc oxide: Vulcanising accelerator in tyre production

Table 4: Example of a template for a declaration analysis (part II): Analysis parameters for waste-derived alternative fuels (Source: MVW)

Declaration analysis (to be completed by the waste producer/waste treatment facility)				
Name of the waste producer/waste treatment facility:				
Number of the analysis[1]:				
Fuel name:				
Date of the analysis:				
	Parameter		**Value**	**Unit**
1.	Net calorific value			kJ/kg
2.	Ash content			mass %
3.	Moisture	H_2O		mass %
4.	Chlorine	Cl		mass %
5.	Fluorine	F		mass %
6.	Sulphur	S		mass %
7.	Cadmium	Cd		mg/kg
8.	Thallium	Tl		mg/kg
9.	Mercury	Hg		mg/kg
10.	Antimony	Sb		mg/kg
11.	Arsenic	As		mg/kg
12.	Lead	Pb		mg/kg
13.	Chromium	Cr		mg/kg
14.	Cobalt	Co		mg/kg
15.	Copper	Cu		mg/kg
16.	Manganese	Mn		mg/kg
17.	Nickel	Ni		mg/kg
18.	Vanadium	V		mg/kg
19.	Tin	Sn		mg/kg
20.	Beryllium	Be		mg/kg
21.	Selenium	Se		mg/kg
22.	Tellurium	Te		mg/kg
23.	Zinc	Zn		mg/kg
24.	Boron[3]	B		mg/kg
25.	Polychlorinated biphenyls[2]	PCB		mg/kg
26.	Lindane[3]	HCH		mg/kg
27.	Benzopyrene[3]	BaP		mg/kg
28.	Pentachlorphenol[3]	PCP		mg/kg

1) alpha numeric with the first two letters of the suppliers
2) sum according to DINx5
3) only for used or waste wood

Possible waste codes for transport and for the delivery

☐ 19 12 10 – Combustible waste (refuse derived fuel)

☐ 19 12 07 – Wood other than that mentioned in 19 12 06

Biologically zinc is one of the most important metals after iron. Zinc is a constituent of many enzymes (e.g. phosphatases, carboanhydrase) and is among the essential trace elements.

4 Investigation of alternative fuels – declaration analysis

Basically, quality management begins with the selection of the suitable waste materials according to the valid guidelines of the cement industry. How can the suitability of a waste material or an alternative fuel from waste be checked?

Each waste material and alternative fuel must be analysed. Apart from the general material composition (water, ash, biologically degradable constituents), the following analyses have to be carried out:

- Elementary analysis: C, H, O, N, S, Cl, F
- Short analysis: Fixed carbon and volatile constituents
- Ash composition
- Mechanical characteristics: Bulk density, particle distribution
- Calorific and reaction kinetic characteristics

A form as shown in Table 1 can be used for the characterisation of alternative fuels

In individual cases further analysis parameters can be required in order to check the suitability of alternative fuels.

As a rule the suppliers of waste-derived alternative fuels have only modest knowledge of the necessary process-specific and pertinent emission protection guidelines for the usage of such waste materials in cement/lime plants. Thus corresponding guidelines need to be laid down and continuously monitored by the cement/lime plant operator within the quality management system. As an example quality guidelines or a specification of combustibles of a cement plant are presented in Table 2.

Most waste-derived alternative fuels consist of material mixtures. The quantitative composition (percentage proportion of the various waste fractions) should therefore be exactly specified as part of a declaration analysis (Tables 3 and 4). This is necessary for process technological reasons in order to assess specifications. It is also partly required by the permitting authorities as often only certain volumes are permitted for each waste type per annum.

In many European countries it has been proved that suppliers of alternative fuels, apart from providing analysis results

Table 5: Example of a "Compliance Confirmation" (Source: MVW)

Compliance Confirmation
Name, address of RDF producer/supplier:
Name:
Street:
ZIP/City:
We herewith confirm that the delivered secondary fuel with the title
conforms to the composition of the declaration analysis number ______ dated ______
Date:
Signature:

of alternative fuels from certified laboratories, also draw up and confirm the above-mentioned declaration analysis. Declaration analyses have to be renewed at certain intervals, e.g. every 1 000 tonnes of fuel supplied.

In addition the suppliers should confirm the validity and compliance of analyses results on each delivery of alternative fuels. This can take the shape of a simple "Compliance Confirmation "as in Table 5.

In this way the cement/lime plant receives an additional legal security in case contrary to contract deliveries occur (faulty loads, contaminated alternative fuels etc.).

5 Final remarks

Comprehensive quality management involves on the one hand the knowledge of the environmentally relevant elements that can occur in the alternative fuels/raw materials. On the other hand samples must be taken regularly in order to make sure that the amount of critical elements in the material does not exceed the limit values. Not only the cement plant itself, but also the producer or supplier of the RDF must be included in the quality control system. Only if the quality management system strictly adheres to this proceeding, can the required high quality of alternative fuels and raw materials be permanently achieved.

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