Perspectives and limits for cement kilns as a destination for RDF

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Abstract

RDF, the high calorific value fraction of MSW obtained by conventional separation systems, can be employed in technological plants (mainly cement kilns) in order to obtain a useful energy recovery. It is interesting and important to evaluate this possibility within the general framework of waste-to-energy solutions. The solution must be assessed on the basis of different aspects, namely: technological features and clinker characteristics; local atmospheric pollution; the effects of RDF used in cement kilns on the generation of greenhouse gases; the economics of conventional solid fuels substitution and planning perspectives, from the point of view of the destination of RDF and optimal cement kiln policy. The different experiences of this issue throughout Europe are reviewed, and some applications within Italy are also been considered.

The main findings of the study are that the use of RDF in cement kilns instead of coal or coke offers environmental benefits in terms of greenhouse gases, while the formation of conventional gaseous pollutants is not a critical aspect. Indeed, the generation of nitrogen oxides can probably be lower because of lower flame temperatures or lower air excess. The presence of chlorinated micro-pollutants is not influenced by the presence of RDF in fuel, whereas depending on the quality of the RDF, some problems could arise compared to the substituted fuel as far as heavy metals are concerned, chiefly the more volatile ones.

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1. Introduction

When choosing the best final destination for solid urban waste, energetic valorisation seems to be, on the one hand, one of the most interesting options given the vast choices of final destinations for this material. On the other hand, this choice involves a debate on the acceptability and compatibility of the technological solutions that are involved, particularly from the point of view of the atmospheric impact.

The present day tendency of planners, particularly in Italy, is to separate a combustible fraction with precisely defined characteristics. Starting from these considerations, there has been a widespread development of urban waste pre-treatment plants in Italy which, once operating, produce a significant amount of the so-called RDF (residue-derived-fuel). The Italian Environmental Protection Agency (APAT) reports that plants in Italy producing RDF have a treatment capacity of more than 7.5×10^6 t/y MSW (APAT, 2004).

The fundamental point from which different views arise and which is the subject of substantial ambiguity within the development plans is what the destination of the produced RDF should be. The waste could be sent to specifically constructed plants in order to obtain thermal energy that in turn would be transformed into electricity for the energy market, or instead it could be utilised as a substitutive fuel material in pre-existing technological plants with remarkable energy consumption capacities. Cement manufacturing plants are of significant importance for this latter purpose if we take into consideration their potential and high temperature conditions that seem to offer a suitable guarantee for thermal destruction.

It is necessary to compare both options for the use of produced RDF. This should be done on the basis of a series of environmental compatibility, economic, and planning criteria, which should obviously be evaluated case by case,

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taking into consideration the local context and the particular issues at play. The present study gives some indications to help guide the choice and evaluate cement kiln options in particular, taking into consideration what the European and non-European technological situations suggest, as well as some particular experience gained in the Italian territory.

2. The utilisation of RDF as fuel material in cement kilns

An alternative to the aforementioned scenario is the development of systems that utilise RDF in cement kilns. These plants have remarkable energy requirements, on the order of 3000–5000 kJ/kg of produced clinker (EU, 2001). Given the high temperatures utilized, these plants would in principle seem ideal for the thermal destruction of residuals without causing adverse environmental impacts.

The operative scheme of a kiln is given in Fig. 1 (Bargagli, 2005). This figure shows how in this case the feed can be partially delivered to the head of the kiln, from which the clinker exits, with the fuel and fumes in a counter-current movement with respect to the movement of the material to be burned. The material could also be delivered in part to the pre-calcinator, which has a different fume residence time and temperature conditions. In the first feed option, the fumes have a residence in the kiln of tens of seconds, and they cross zones where the temperature is higher than 1500 °C. In the second case, the temperature is 800–900 °C in the introduction zone, and the residence times of the fumes in the thermal recovery zone (with gradually decreasing temperatures) do not exceed several seconds. This obviously has important consequences on the possible reactions in the gas phase.

As far as the emissions into the atmosphere are concerned for this system, it is not easy to distinguish between the contribution of the clinker production process and the contribution of the RDF. This issue is where attention should be concentrated.

As far as the generic emission of combustion products from cement kilns is concerned, some indications concerning the main products of combustion (CO_2, CO, powders, NO_X, and SO_2) have been reported in the BREF documents (EU, 2001).

As for the specific contribution of waste combustion, this can be well represented by the possible formation of dioxins that can derive from specific precursors present to a significant degree in the combustible materials. Some of these aspects will be addressed later in the paper.

3. International situation of cement kiln co-incineration (use of secondary fuels)

In Europe, the cement industry is a large consumer of secondary fuels, with more than 100 kilns across Europe co-incinerating different types of materials (see Table 1, European Commission, 2003).

Some studies reported 1.8 million t/y of secondary fuels co-incinerated in cement kilns in Europe in 1997, which is expected to increase by 15% by 2003. The related strategy for the cement industry is to rely on alternative fuels to reduce its high energy bill (energy costs typically represent 30–40% of manufacturing costs of Portland cement), as well as for sustainable development. This is also an important consideration from the point of view of carbon dioxide emissions and the consequent possibility to benefit from carbon emission credits.

Hazardous wastes (1 million t/y) and tyres (550,000 t/y) are the most frequently used secondary fuels. However, future attention should be switched to biomass-based fuels including wastepaper and sewage sludge for carbon emission credits.
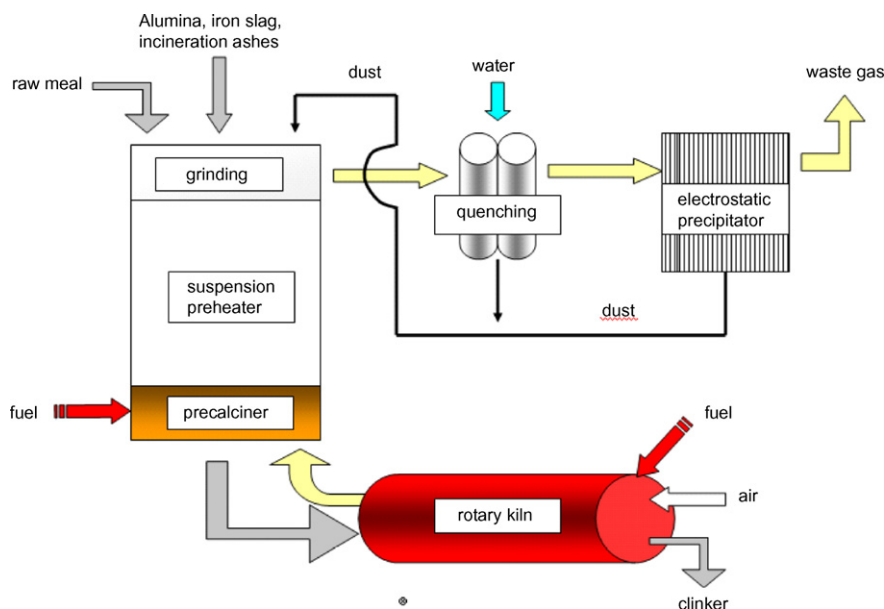

Fig. 1. Diagram of a cement kiln with a pre-heater and pre-calciner.

Table 1
Quantities of RDF co-incinerated in the cement industry in Europe ($\times 10^3$ t/y)

Secondary fuels	AT	BE	DK	Fl	FR	DE	GR	IR	IT	LU	NL	PO	ES	SE	UK	Total
Tyres	30	25		8	200[e]	240			i		–	6.5	13		25	550
Waste oil	30	b,i			520[b,e]	180							9	6	120	1000
Solvent	7.5					25					10					
Sewage sludge		15	7.5								30					50
Plastics/paper	25	i	10			290										350
Bone meal/animal fat	10	220			100				i							350
Wood			>0.5			80							2+5[g]			100
Other	40[a]	c,i	22[d]			115				>5[f]			10		h,i	200
Total	142.5	NI	40	8	820	930	0	0	(NI)	(NI)	>45	6.5	39	6	(>55)	2600
Substitution rate (%)	26	40	7		24	23			1.5	5–10			1.2	13		

Notes:
Figures in brackets are quantities which have been reported incomplete.
[a] Paper fibre residues.
[b] Mainly reconstituted fuel mixed with sawdust or other absorbent matter.
[c] Including automative shredder residues and carpet/textile pellets.
[d] Including waste textiles and unspecified non-hazardous wastes.
[e] Estimates.
[f] Including paper sludge and waste rubber.
[g] Sawdust.
[h] Profuel derived from a variety of sources including paper, plastics and carpet cut-offs.
[i] Quantities were not available.

Other wastes are co-incinerated in cement kilns in Europe. Examples include mainly commercial and industrial waste packaging (350,000 t/y of paper and plastics rejects), bone meal (350,000 t/y), and sewage sludge (50,000 t/y).

The European energy substitution rate for secondary fuels in the cement industry led to a fuel usage (average in Europe) of about 10%, compared with 39% of pet coke, 42% of coal, and 9% of fuel oil and gas in 1995.

Different countries had different rates of thermal substitution, from 72% in The Netherlands to 2% in Spain, including 30% in Germany and 5% in Italy.

A technical-economic study referring to the prospects for the UK cement industry recently estimated, depending on cement production growth (with an expected range of variation from 0% to 2%), energy efficiency improvements, thermal substitution from 5% to 10%, and the use of substitute residue fuels from 125,000 to 600,000 t/y (Juniper Consultancy Service Ltd., 2005).

In Italy, there have been two principal experiences with the use of RDF in cement kilns. In 2005, the Holcim group in Lombardia was authorized to use 15,000 t/y of RDF for one plant (Merone) and 60,000 t/y of animal meal together with 130,000 t/y of fossil fuels for another plant (Ternate).

The other experience, the Buzzi Unicem cement kiln in Piedmont, will be described in more detail later. The most important aspect of this case is that of the three rotary kilns in the plant, the biggest one (3500 t/d of clinker) used a thermal substitution of 24.5% in 2004, and the second (1900 t/d) had a thermal substitution of 7%.

4. Technological aspects

Leaving the discussion on environmental aspects for the following section, the substitution of secondary fuels for conventional fossil fuels in cement kilns must be evaluated from the technological point of view, starting by considering the energy and mass balances of the substitution.

Concerning this first point, it must be taken into account that some solid fuel substitutes present a lower calorific value (CV) in comparison with conventional ones (pet coke, as an example). In comparison with 34,000 kJ/kg, RDF presents a CV in the range of 15,000–20,000 kJ/kg. Sludge has a lower value, and only mixing with plastics or rubber can increase this value. Therefore, calorific substitution can only be obtained with a higher fuel flow rate. By defining CV as the calorific value and α as the stoichiometric air consumption as well as the same air excess in the case of conventional or substitute fuels, the ratio between the gas flow rates can be expressed as

Gas flow rate = $k\, CV/\alpha$.

Hypothetically considering pet coke (with composition C 86%, H 3.65%, N 2% and S 5%) with a calorific value of 33,000 kJ/kg and a primary air requirement of 9.4 Nm^3/kg (9.16 Nm^3/kg of stoichiometric dry waste gas, 0.41 Nm^3/kg of steam), and RDF (with composition C 53%, H 7%, O 21%, inorganic 19%) with a calorific value of 20,000 kJ/kg and an air requirement calculated as 6.16 Nm^3/kg (5.92 Nm^3/kg of stoichiometric dry waste gas, 0.78 Nm^3/kg of steam), the substitution of RDF for pet coke leads to an increase of more than 15% in the produced waste gas in wet conditions (from 0.29 Nm^3/MJ to 0.335 Nm^3/MJ).

The use of RDF as an alternative fuel, in a system with a constant blower capacity and a limited amount of fumes that can be emitted, can be managed in two different ways. First, the same thermal conditions, i.e., the same temperature profile, can be maintained, by providing a smaller

amount of secondary air (the percentage of oxygen in the dry fumes will be smaller). Second, the same dilution factor can be maintained, resulting in the same oxygen concentration in the waste gas and a lower combustion temperature. Both of these choices can lead to a smaller formation rate of NO_X.

From the point of view of composition, it is important to consider the presence of nitrogen, sulphur, and chlorine in substitute fuel in comparison with the reference concentrations of fossil fuels. The nitrogen is responsible for the formation of nitrogen oxides. Low values in RDF (0.3–0.5% in comparison with 1.5–2% in fossil fuels) can lead to lower formation of these harmful products.

In general, the formation of NO_X is related to the amount of nitrogen in the fuel, the temperatures in the kiln, the residence times, and the types of burners. It is difficult to forecast and model all of these aspects together, but it can be accepted that there will be a lower concentration in the off-gases when RDF is used. Some implications of this issue will be discussed in the following sections.

Due to the alkaline matrix of the clinker, the presence of sulphur and chlorine in substitute fuels does not result in critical levels of gaseous emissions. On the contrary, the possibility of reactions of these elements with different metals in raw meal must be considered.

The concentration of sulphur in substitute fuels is generally much lower than the reference value in conventional fossil fuels (0.1–0.2% in RDF, 3–5% in fossil fuels). Therefore, any problems regarding precipitation or clogging can be excluded, although issues of alkali sequestration and transfer in the clinker must be verified.

On the contrary, an increase in chlorine (0.3–0.5% in RDF, very low values less than 0.1% in coke) can lead to some problems arising from reactions between alkali and chlorine, the volatilisation of chlorides and recycling with dust, and the necessity to operate a bypass (extraction of part of the flue-gas) in order to limit the chlorides in the final clinker (Kurdowski, 1983). There are reliable indications that the high temperature of bypassed gases causes an increase in heat consumption. Each percentage of bypassed gases requires approximately 20–25 kJ/kg of clinker, compared to a total consumption of 3000–3500 kJ/kg in the cement kiln. As the indicated order of magnitude is 5–15%, this aspect can contribute significantly to the total heat requirement of the system.

The presence of heavy metals in secondary fuels can lead to a transfer in the produced clinker. There are some indications in the literature about this transfer, which must be compared with the avoided transfer from fossil fuels. As the presence of different metals is not the same in different fuels, the level of contamination of the clinker can increase or decrease after fuel substitution. For example, cadmium clinker enrichment is strongly dependent on secondary fuels. Arsenic, on the other hand, is chiefly present and transferred from conventional coal. A general scheme of the origin of heavy metals can be observed in Forshungzentrum Karlsruhe in der Helmhotz-gemeinschaft (2003).

The possibility of the transfer of these metals to the environment during use (leaching) or during the recycling or reuse of concrete residuals has been considered. Some experimental results indicate limited possibilities for transfer due to the phenomena of crystallisation during concrete preparation and cement aging and of the pH of the microenvironment. Consequently, the transfer of heavy metals from secondary fuels is not critical.

A final important aspect for the proposed substitution of secondary fuels is the low density of this material in comparison with conventional fuels. Taking into account the transport and storage costs, the cost of substituted fuels per unit of heat produced is higher than the cost of coke or coal.

5. Global effects for the two layouts

The decision between RDF combustion in a plant set up specifically for this purpose or in a cement kiln should consider, as a first element of evaluation, the effect of the different final destinations on pollutant emissions and environmental compatibility. This evaluation must take place on a global scale, examining greenhouse gases and CO_2 emissions in particular, and on a local or regional aspect, taking into account the emission of macro-pollutants (NO_X, HCl, and PM) and micro-pollutants (PCDD/F, heavy metals). Therefore, the environmental compatibility in terms of induced toxicity must be distinguished between these two scales.

As far as the global aspect is concerned, the data reported by the European Commission (2003) in Table 2 illustrate the contribution that the utilisation of a unit of RDF supplied to a cement kiln or to a combustion system for energetic purposes makes to global warming, to photochemical smog, to acidification, and to the consumption of resources. It should be noted that these results take into consideration the different steps in the use of the RDF from production to utilisation. The CO_2 emissions data appear particularly significant, indicating that this is the most important contribution of the system with respect to the Kyoto parameters. The use of RDF in cement manufacturing kilns seems to be positive, as the combustion of RDF allows for a reduction of about 1.61 kg of CO_2 per kg of utilised RDF compared to conventional combustible materials (coal). This is due to the chemical composition of the combustible material. When RDF is used in specifically set up combustion systems with energetic recovery, taking into consideration the energetic mix for the production of electric energy and the efficiency of the electric production, the substitution of the combustible material involves an increase in the production of CO_2 of about 0.15 kg per kg of RDF.

As previously mentioned, the cement industry claims that burning RDF instead of coal or pet coke yields advantages for parameters like NO_X and SO_X due to the different elemental composition of the fuels and the different burning conditions. The benefit derived from the use of RDF

Table 2
Results of the impact assessment of 4 technical options for burning 1 mg RDF

		Brown coal fired power plant		Hard coal fired power plant		Cement work		MSWI	
		RDF	Subst. fuel (brown coal)	RDF	Subst. fuel (hard coal)	RDF	Subst. fuel (hard coal)	RDF	Subst. electricity mix
Fossil resources									
Raw oil	kg	5.03E+00	1.22E+00	5.22E+00	5.80E+00	2.17E+01	2.28E+01	4.64E+00	7.80E−01
Natural gas	kg	3.60E+00	3.17E+00	4.33E+00	1.16E+00	8.34E+00	5.50E+00	4.14E+00	1.13E+01
Hard coal	kg	2.15E+01	1.69E+00	2.14E+01	5.70E+02	3.70E+01	5.84E+02	2.16E+01	4.70E+01
Brown coal	kg	6.40E+01	1.33E+03	6.32E+01	5.09E+00	1.05E+02	5.38E+01	7.04E+01	1.78E+02
Total (CED)	kJ	1.88E+06	1.78E+07	1.74E+06	1.62E+07	3.17E+06	1.78E+07	2.10E+06	3.36E+06
Global warming									
CO_2 (fossil)	kg	4.75E+02	1.71E+03	4.72E+02	1.47E+03	2.46E+03	3.93E+03	4.79E+02	3.29E+02
CH_4	kg	3.27E−01	2.48E−02	3.31E−01	6.89E+00	7.46E−01	7.41E+00	3.28E−01	6.41E−01
N_2O	kg	1.15E−02	5.08E−02	3.82E−02	2.98E−02	1.53E−02	1.01E−02	1.44E−02	4.18E−03
GWP	kg CO2-Eq	4.85E+02	1.72E+03	4.91E+02	1.62E+03	2.48E+03	4.09E+03	4.91E+02	3.44E+02
Summer smog									
CH_4	kg	3.27E−01	2.48E−02	3.31E−01	6.89E+00	7.46E−01	7.41E+00	3.28E−01	6.41E−01
NMVOC	kg	3.67E−01	6.17E−02	3.67E−01	6.33E−02	3.63E−01	6.08E−02	3.17E−01	1.07E−02
NO_X	kg	1.24E+00	1.24E+00	1.14E+00	1.18E+00	6.85E+00	7.21E+00	1.11E+00	4.69E−01
NCPOCP	kg	4.22E−01	1.79E−01	4.05E−01	2.97E−01	1.03E+00	7.89E−01	3.69E−01	6.47E−02
Acidification									
SO_2	kg	6.38E−01	1.37E+00	1.01E+00	1.47E+00	1.01E+00	1.00E+00	6.19E−01	2.55E−01
NO_X	kg	1.24E+00	1.24E+00	1.14E+00	1.18E+00	6.85E+00	7.21E+00	1.11E+00	4.69E−01
NH_3	kg	2.06E−01	1.76E−01	1.04E−01	4.44E−02	6.16E−02	9.55E−04	7.82E−02	2.95E−03
HCl	kg	3.82E−01	8.75E−01	4.27E−01	7.52E−02	3.36E−02	2.05E−02	2.89E−02	1.06E−02
HF	kg	2.68E−03	5.94E−03	2.68E−03	2.41E−03	4.51E−03	2.46E−03	4.92E−03	1.50E−03

has been quantified by the European Commission (2003) as 0.36 kg NO_X/t of burned RDF.

6. Local effects of the two layouts

The negative impact of the emission of atmospheric pollutants from the raw composition of burned RDF consists of the possible transfer of substances contained in the waste to the atmosphere or the produced clinker. In the case of incineration, the possible transfer is towards either the atmospheric flow or residuals from the treatment of the fumes.

The European Commission (2003) reports some interesting figures about this transfer phenomenon. The combustion of 1 t of RDF in a cement kiln, if compared to the use of hard coal, causes an increase of around 421 mg in the emission of mercury, 4.1 mg of lead, and 1.1 mg of cadmium.

The transfer coefficients in the case of specific RDF incineration (data from 23 waste incineration plants in Germany, Switzerland, The Netherlands, and Austria) and those from RDF use in cement kilns (data from Germany, USA, Austria, Switzerland, and Portugal) are shown in Table 3 (EEB BZL, 2001; LCA IWM, 2005).

The compared figures (TF for RDF) show clearly higher chlorine and sulphur releases into the atmosphere in the case of co-combustion, along with the fact that the heavy metal retention capacity of the treatment systems for incineration appears to be much higher than those seen in co-combustion systems. In the case of incineration, the complementary quantity of the emitted substance is therefore retained and incorporated into a matrix that consti-

Table 3
Transfer factors to waste gas for RDF contaminants, in the case of incineration and co-combustion in cement kilns

	Transfer factors (TF) for RDF		Transfer factors (TF) for waste solvents
	TF to waste gas for incinerators (%)	TF to waste gas for cement kilns (%)	TF to waste gas for cement kilns (%)
Chlorine	0.08	3.4	–
Sulphur	0.1	3.1	–
Cadmium	0.5	1.873	4.32
Thallium	0.065	0.875	2.81
Mercury	5	49	24.96
Antimony	0.004	0.042	–
Arsenic	0.001	0.020	0.01
Lead	0.005	1.015	0.21
Chromium	0.005	0.018	0.01
Cobalt	0.005	0.014	–
Copper	0.005	0.040	0.01
Manganese	0.005	0.010	–
Nickel	0.005	0.019	0.001
Vanadium	0.005	0.050	–
Tin	0.005	0.043	–
Zinc	No data	0.437	0.18

tutes a hazardous residual, which is then treated with specific inactivation treatments. In the case of co-combustion, the transfer occurs towards the clinker with a greater possibility of later transfer into the environment.

The reported transfer factors for cement kilns can be compared to other transfer coefficients (reported in the last column of Table 3) found for the use of waste solvent in

Swiss cement plants (Seyler et al., 2004). As can be easily seen, the order of magnitude, particularly for the most volatile elements (Hg, Tl, and Cd), is confirmed. Moreover, the European Recovered Fuel Organisation (Tubergen et al., 2005) reports transfer factors in the range of 10–40% for mercury, 0.48% for Cd + Tl, and 0.02% for the remaining heavy metals.

In the case of co-combustion of RDF in a cement factory, it is very important to understand the possible change in the emissions values and the produced clinker in comparison with the levels usually associated with the use of pet coke or coal. The comparison is obviously based on the actual caloric substitution and the calorific value of the RDF. The concentrations of heavy metals in RDF or in traditional fuels are quite variable, as indicated in the literature. Table 4 reports a summary of a very large database on the contamination of RDF. The data are taken from the final report of the European Commission (2003), from the study of the European Recovered Fuel Organisation (Tubergen et al., 2005), from EEB BZL (2001), and from a private analysis on high quality RDF produced in Italy.

As far as traditional fuels are concerned, the concentrations of the heavy metals can be taken from the data reported for five Swiss plants (Seyler et al., 2004), from some reports by the Portland Cement Association (PCA, 2003), from Zevenhoven and Kilpinen (2001), the Society of Petroleum Engineers (2003), Husar and Husar (2001), AES DRAX (2002) and the EPA (2001). Table 5 shows the range defined by the referred data.

The reported data have been used to carry out a comparison based on the calorific value of materials and the possible caloric substitution in a cement kiln, as indicated by Table 6. The last two columns are derived from a study published by the German cement work association (Verein

Table 5
Characteristics of traditional fuels for cement work

	Coal		Pet coke	
	Min	Max	Min	Max
N (%)	1.3	1.3	2	2
S (%)			5	5
Cl (%)			0.01	0.01
CV (kJ/kg)	23,220	33,040	33,863	33,863
Sb (ppm dry)	1	1	0.2	0.2
As (ppm dry)	0.5	10	0.46	0.46
Cd (ppm dry)	0.05	10	0.1	0.3
Cr (ppm dry)	0.5	60	2	104
CrVI (ppm dry)				
Co (ppm dry)	0.5	20		
Mn (ppm dry)	5	300		
Hg (ppm dry)	0.02	4.4	0.02	0.1
Ni (ppm dry)	0.5	100	200	300
Pb (ppm dry)	1	300	2.4	100
Cu (ppm dry)	5	60		
Sn (ppm dry)	10	10		
Tl (ppm dry)	1	1	0.04	3
V (ppm dry)	1	100	400	2342
Zn (ppm dry)	1	1000	6.8	6.8

Deutscher Zementwerke). As can be easily observed, RDF usually has a higher content of Sb, Hg, Cd, As, Pb, Cu, Cr and Zn than the pet coke. However, coal can sometimes also present large amounts of Hg, Co, Cd and Tl.

Based on these data and the transfer factors reported in Table 3 (TF to waste gas for cement kilns), a simulation has been performed of the effect of the use of RDF instead of coal and pet coke (50% of caloric substitution has been assumed) on the emissions of a cement kiln. Table 7 and Fig. 2 report the results and show that the substitution of pet coke with RDF has a negative impact on heavy metal emissions, particularly for mercury, whereas a positive effect can generally be expected if RDF is used instead of coal. Anyway, for this simulation, all of the predicted values comply with the existing emissions limits.

The same simulation can be done using the composition of fuels, traditional and alternative, provided by the German cement work association (VDZ) and reported in Table 3. The results are summarized in Table 8 and Fig. 3. In this case, it is evident that the use of alternative fuels can strongly worsen the emission of heavy metals, pushing them dangerously towards the limits.

However, it is important to confirm that the composition of RDF can be quite variable, as can be observed from the data reported by Zevenhoven and Kilpinen (2001): Hg concentrations from 1 to 10 ppm, instead of the assumed range of 0.1–0.4 ppm, and Cd concentrations from 1 to 10 ppm instead of 0.18–2.6 ppm. Obviously, these concentrations could change the results reported and lead to different conclusions. This is particularly true for mercury, which would exceed the limit.

In any case, it is evident that the use of RDF instead of traditional fuels in a cement kiln could be dangerous in terms of the presence of larger amounts of heavy metals in the waste gas, so the quality and the quantity of RDF

Table 4
Composition of RDF, including heavy metals

	Min	Max	Italian law reference	
			RDF	High quality RDF
N (%)	0.52	0.52		
S (%)	0.1	0.2	0.6	0.3
Cl (%)	0.28	0.7	0.9	0.7
CV (kJ/kg)	13,000	22,000	15,000	20,000
Humidity (%)	2.9	34	25	18
Sb (ppm dry)	9	14.7		
As (ppm dry)	0.9	8.8	9	5
Cd (ppm dry)	0.18	2.6	<7	3
Cr (ppm dry)	11.3	140	100	70
CrVI (ppm dry)				
Co (ppm dry)	0.6	4		
Mn (ppm dry)	28	210	400	200
Hg (ppm dry)	0.1	0.4	<7	1
Ni (ppm dry)	0.85	21	40	30
Pb (ppm dry)	25	157	200	100
Cu (ppm dry)	45	266	300	50
Sn (ppm dry)	4	500		
Tl (ppm dry)	0.02	0.5		
V (ppm dry)	0.3	7		
Zn (ppm dry)	225	340		

Table 6
Comparison between traditional and alternative fuels

	Range RDF		Range coal		Range pet coke		VDZ (max values)	
	Min (mg/MJ)	Max (mg/MJ)	Min (mg/MJ)	Max (mg/MJ)	Min (mg/MJ)	Max (mg/MJ)	Fuels (mg/MJ)	Alternative fuels (mg/MJ)
Sb	0.419	0.685	0.036	0.036	0.006	0.006	0.07	0.05
As	0.042	0.410	0.018	0.355	0.014	0.014	1.9	1
Cd	0.008	0.121	0.002	0.355	0.003	0.009	0.3	0.7
Cr	0.527	6.524	0.018	2.133	0.059	3.071	3.7	21
CrVI								
Co	0.028	0.186	0.018	0.711			1.2	8
Mn	1.305	9.786	0.178	10.665				
Hg	0.005	0.019	0.001	0.156	0.001	0.003	0.06	0.1
Ni	0.040	0.979	0.018	3.555	5.906	8.859	3.5	25
Pb	1.165	7.316	0.036	10.665	0.071	2.953	10	25
Cu	2.097	12.396	0.178	2.133			3.7	67
Sn	0.186	1.282	0.355	0.355			0.4	0.7
Tl	0.001	0.023	0.036	0.036	0.001	0.089	0.15	0.1
V	0.014	0.326	0.036	3.555	11.812	69.161	6.7	16
Zn	10.485	15.844	0.036	35.549	0.201	0.201	8	625

Table 7
Emissions of heavy metals due to different fuels fed to a cement kiln

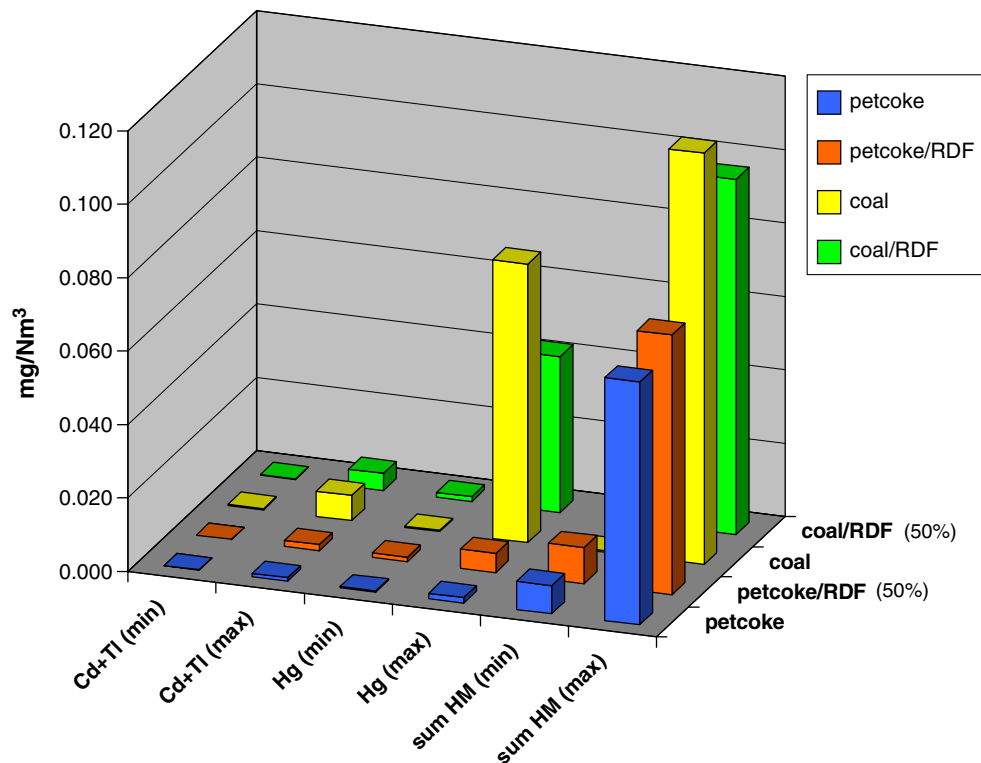|	100% pet coke	50% pet coke 50% RDF	100% coal	50% coal 50% RDF	Limits (mg/Nm^3) incineration directive
Cd + Tl min (mg/Nm^3)	0.00006	0.00011	0.00034	0.00025	0.05
Cd + Tl max (mg/Nm^3)	0.00093	0.00169	0.00690	0.00467	
Hg min (mg/Nm^3)	0.00029	0.00127	0.00034	0.00130	0.05
Hg max (mg/Nm^3)	0.00143	0.00524	0.07588	0.04246	
Sum HM min (mg/Nm^3)	0.00769	0.00984	0.00049	0.00673	0.5
Sum HM max (mg/Nm^3)	0.06613	0.07076	0.11206	0.09668	

Fig. 2. Emissions of heavy metals due to different fuels fed to a cement kiln.

Table 8
Emissions of heavy metals based on the data provided by VDZ

	100% traditional fuels (mg/Nm^3)	50% alternative fuels (mg/Nm^3)	Limits (mg/Nm^3)
Cd	0.005563	0.0093	
Tl	0.001299	0.0011	
Cd + Tl	0.0069	0.0104	0.05
Hg	0.029106	0.0388	0.05
Sb	0.000029	0.00002	
As	0.000376	0.00029	
Pb	0.100485	0.1758	
Cr	0.000659	0.0022	
Co	0.000166	0.0006	
Cu	0.001465	0.0140	
Mn			
Ni	0.000658	0.0027	
V	0.003317	0.0056	
Sum HM	0.1072	0.2013	0.5

Table 9
Maximum possible concentrations in SRF, cement kiln dry process

	TF	Ce (WID) (mg/Nm^3)	C max – calculated (mg/MJ)
Hg	0.1–0.4	0.05	0.082–0.33
Cd + Tl	0.0048	0.05	6.90
Sum HM	0.0002	0.50	1650

Notes: (1) Vs = 0.66 m^3/MJ.
(2) Ce at 10% O$_2$.

to be burned should be analysed in depth. The European Recovered Fuels Organisation recommends maximum concentrations of heavy metals in solid fuels (SRF) in order to comply with emissions limits (Tubergen et al., 2005) for a dry cement kiln process (see Table 9).

It is important to underscore that the transfer factors can change according to the composition of the fuel (for example, which molecules mercury forms around), to the presence of halogens (for example, Pb, Ag, Ni are much more volatile as chlorides) and to the occurrence of a reducing or oxidising atmosphere. Another factor that
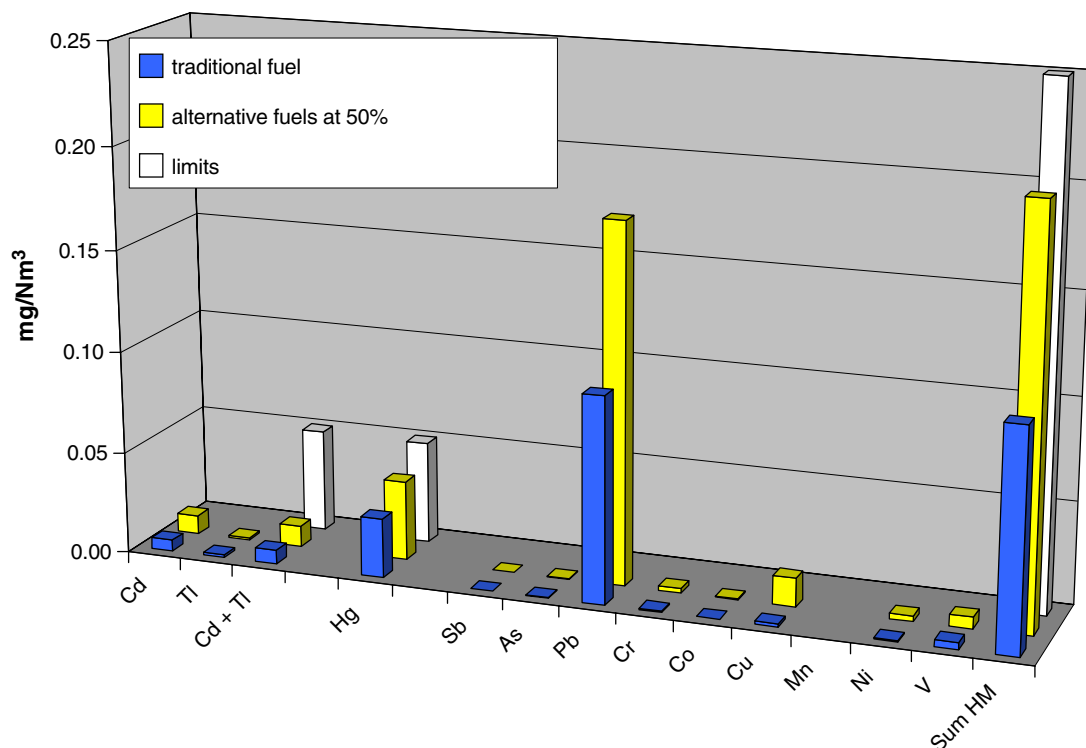
can influence the transfer factors is the dedusting system of the kiln, usually an electrostatic precipitator (ESP), which can remove part of the metals that are present in particle form at exhaust gas temperatures. The separated dusts are generally recycled in the raw meal so that an internal cycle of heavy metals is realised. If the ESP is substituted by a fabric filter with a higher separation efficiency, the transfer factors can change as the concentration of the heavy metals recycled to the system grows. Consequently, their vapour pressure in the waste gas may also become larger. This can lead to a different solid/gas equilibrium, with different boiling points and different transfers of heavy metals towards the clinker or emissions.

On the basis of the main findings reported in the present section, the transfer factors of heavy metals should be defined case by case by means of precise analyses of traditional fuels, RDF, raw materials and the produced clinker. After this, the amount of alternative fuels to be used in the studied cement kiln can be decided.

Fig. 3. Emissions of heavy metals based on the data provided by VDZ.

7. Formation of micro-pollutants

As far as the possible formation of dioxin is concerned, a complete study has been conducted on the emissions from the co-combustion system (SINTEF, 2004). The main results of this study are as follows:

- there is no correlation between dioxin emissions and the type of alternative combustible material used (Fig. 4);
- the formation of dioxins can occur in a thermal window between 200 and 450 °C, zones that are encountered in fume cooling systems before the final separator of the fumes;
- potential precursors released by combustible material introduced into the pre-calcination zone can react with the chlorine not retained by the alkaline matrix of the clinker, in the presence of metallic catalysts present in the transported powders, giving rise to emissions of dioxin where de-novo synthesis occurs;
- while the dioxin concentrations are, in most cases, lower than 0.1 ng/Nm^3, concentrations of PCB at least a thousand times higher are possible. In this sense, they constitute a significant source of precursors that are able to generate micro-pollutants where the aforementioned kinetic conditions allow this to happen.

Based on our experience, some problems can arise for cement kilns when using secondary raw materials containing micro pollutants or precursors (PCB, PAH). In this case, the pre-heater of the kiln presents temperatures and residence times suitable for volatilisation of dioxin and chloro-aromatics, as well as for the so-called de novo synthesis from organics contained in the feed.

A final consideration should be made concerning micro-pollutants. It would be more appropriate to talk in terms of mass fluxes rather than emissions concentrations. In fact, in an incineration system, the combustion of 1 kg of RDF produces 5 Nm^3 of fumes with a PCDD/F concentration lower than 0.1 ng/Nm^3, a specific emission of 0.5 ng PCDD/F/kg RDF. On the other hand, considering a 20% substitution rate of the combustible material by wastes in a cement kiln, 30 g of supplied RDF produce an emission of 3 Nm^3 of fumes with a PCDD/F concentration below 0.1 ng/Nm^3, a specific emission of 10 ng PCDD/F/kg RDF. Obviously, it is not possible to say that all of the possible dioxins derive from the RDF. However, if this were taken to be true, the specific generation capacity of the co-combustion systems in cement kilns would be decidedly higher.

8. Economic aspects and planning

Apart from the point of view of atmospheric impact, the different solutions of disposal in co-combustion systems should also be compared from the operational cost point of view. As far as combustion in cement kilns is concerned, the costs have to be defined case by case, taking into account the following items:

- the ratio of calorific power of the substituted combustible to the RDF;
- the market cost of the substituted fuel;
- the difference between the operational cost of the kiln in a conventional setup and using RDF;
- the cost or entrance taxes for the substitute fuel.

As far as these items are concerned, many factors must be taken into account, including the constant increase in costs of the combustible market, the possible increased importance of emissions trading due to the application of the Kyoto protocol, the greater plant treatment and maintenance costs which a substitutive combustible involves, the competition from other potentially combustible residuals, the costs avoided due to the different destinations of the RDF, and the policies for the incentives related to renewable energy sources.

Another aspect of fundamental importance is the prospective planning and the ease of use of the RDF. It is necessary to consider the potential of the installed cement production plants and of their RDF acceptance capacity. As an example in the Italian territory, there are about 60 plants and 80 kilns for the production of cement (Ministero dell'Ambiente e Tutela del Territorio, 2006) which accounts for over 40×10^6 t/y. Assuming a specific energy consumption of 4×10^3 kJ/kg in clinker production kilns and a calorific power of the RDF of 15×10^3 kJ/kg, about 107×10^3 t/y of RDF can be supplied to cement plants for each percentage point of caloric substitution. The contribution to the disposal and valorisation of waste using a technology involving very few transformations and already available on the territory is immediately obvious.

It is also essential to take into account the constraint that the prospect of a supply contract for RDF imposes on the producer or public holder of this type of material concerning its final use, the possible competition of other types of alternative combustible materials on the market,
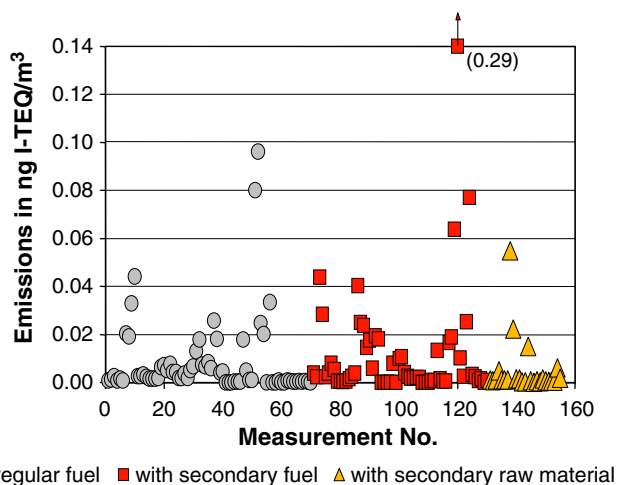
Fig. 4. PCDD/F emissions of German cement kilns between 1999 and 2002.

Table 10
Specific emissions with different caloric substitutions

	Forno 1	Forno 2	Forno 3
POWER (MWt)	40	80	145
Substitution (%) with alternative fuels	0	7	24.5
NO_X (g/kg clinker)	4.07	2.84	2.72
SOx (g/kg clinker)	0.079	0.035	0.048
COV (g/kg clinker)	0.017	0.011	0.023
CO (g/kg clinker)	2.96	0.87	0.50
Dust (g/kg clinker)	0.065	0.015	0.020

and potential local reactions to the alteration of a production plant to a plant involved in the disposal of urban waste.

These aspects must be evaluated case by case taking into consideration the dimensions of the problem, the local industrial structure, the energy market, and the suitability of the solutions.

9. A local case in Piedmont, Italy

In the province of Cuneo (northwest Italy), significant experience was gained through a collaboration between an important cement manufacturer and the Waste Disposal Company in Cuneo in the southern part of Piedmont, Italy. A total of 25,000 t/y of material known as RDF-P (calorific power >4500 kcal/kg, moisture <10%, total chlorine <0.5%, PCB-PCT <5 ppm, PAH <5 ppm, Cd <100 ppm, Hg <10 ppm, Zn <5000 ppm, Pb <2000 ppm, etc.) is produced from urban waste gathered in the city of Cuneo after mixing with plastic and rubber residuals.

The substitution was carried out in two kilns in the plant, one with a capacity of 145 t/h of clinker ("forno 3") and the other with a capacity of 79 t/h ("forno 2"). The caloric substitutions were around 24.5% and 7%, respectively, in 2004. The highest possible energetic substitution is 40% in the kiln (temperature >1450 °C, with excess air in the range of 1.10–1.15, retention time >2 s) and 50% in the precalciner (temperature >850 °C, with excess air in the range of 1.10–1.15, retention time >2 s). Comparing the emissions of the third kiln ("forno 1") of the same cement factory, where only coal is used as the combustible material, with those of the other two kilns, where an important quantity of alternative combustible materials is used, it can be easily noticed that the co-incineration practice does not seem to affect the quality of the emissions, at least from the point of view of macro-pollutants (NO_X, SOx, VOC, CO, and dust). Table 10 reports this data in detail.

10. Conclusions

This paper has shown that the use of RDF in cement kilns is a real technological solution both for RDF producers, urged to find a useful final destination for the produced material, and for cement plant operators, whose first objectives are the economics of production, optimal energy allocation, and limiting environmental impact.

In many countries, chiefly in Northern Europe but increasingly in all EU countries including Italy, this practice is being carefully considered and implemented as part of the general operation of using substitute fuel. There are some limitations arising from low calorific value and the chemical presence of atmospheric pollutant precursors, but there are also positive trends related to the low cost of RDF, large production capacity, and territorial distribution.

Issues involving kiln thermal and mass balances are very important as they can limit the RDF substitution rate, and, in some cases, technological modifications and process parameter adjustments are required. It is a specific task for kiln operators to define the real possibility of substitution by evaluating the quality and thermal characteristics of RDF as the basic parameters to define the compatibility at fixed substitution ratios.

– From the point of view of environmental performance, different conclusions can be drawn:
– The substitution of RDF for coal or coke has a positive effect on greenhouse gas formation over traditional schemes. Apart from the contribution to meeting Kyoto parameters, this can correspond to economically positive aspects through emissions trading.
– The formation of conventional gaseous pollutants is not a critical aspect, as sulphur and chlorine are well retained by the alkaline micro-environment. The elimination of suspended fine dust is a traditional operation of cement kilns, and the generation of nitrogen oxides can probably decrease due to lower flame temperatures or lower excess air.
– Some danger could arise as far as heavy metals are concerned, chiefly the more volatile ones, due to their presence in the substitution fuels and their transfer factors to gaseous emissions. RDF usually has a higher content of Sb, Hg, Cd, As, Pb, Cu, Cr and Zn than pet coke, but sometimes coal can also present large amounts of Hg, Co, Cd and Tl. In this way, the compatibility of RDF as a fuel depends on its quality. The transfer factors can be very plant-specific and should be determined case-by-case.
– The presence in atmospheric emissions of chlorinated micro-pollutants is not influenced by the presence of RDF in fuel, due to the high thermal destruction capacity of the kiln. Compliance with common standards for this type of pollutant is not difficult. The mass fluxes of micro-pollutants and their origin are not yet completely defined and must be further examined.

On the basis of all of these considerations, taking into account the absolutely critical aspects of the RDF market in Italy and the high contribution of the cement industry to carbon dioxide emissions, this option must be considered in the planning of territorial systems. This is not necessarily intended as a general solution, but as a useful aid for actual environmental problems.

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