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Self-propagating reactions for environmental protection: state of the art and future directions

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Abstract

The major achievements obtained in the field of self-propagating reactions exploited for environmental protection are reviewed. In particular, the fixation and consolidation of high level radioactive wastes (RAWs), the treating and recycling of a highly toxic solid waste from electrolytic zinc plants, the recycling of silicon sludge and aluminum dross produced by semiconductor industries and aluminum foundries, respectively, and the degradation of chlorinated aromatics are addressed. Future scientific and technological directions related to this promising field of reaction engineering are foreseen. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Integrated environmental protection can be implemented in the process industry as well as energy conversion plants by process redesign, reutilization of residues and safer disposal of wastes with the aim of reducing and avoiding pollutants. Process innovation (i.e. production of the same or similar products using less raw material and energy and decreasing the pollutant output), materials cycles (i.e. recycling of residues and produced wastes so that resources are reduced) and safe waste disposal [1], represent the characteristic elements of a sustainable development model. In this work, we address the use of self-propagating reactions for residues recycling and environmentally benign waste disposal.

It is well known that self-propagating reactions of either solid–solid and gas–solid type have been exploited in the establishment of the technique referred to in the literature with the acronym of self-propagating high-temperature synthesis (SHS) which represents an attractive alternative to conventional methods of materials synthesis. This technique is characterized by the fact that once the starting mixture is ignited by means of external thermal sources for relatively short times, highly exothermic reactions may propagate through the mixture in the form of a self-sustained combustion wave leading to final products progressively without requiring additional energy, as depicted in Fig. 1 [2–6]. SHS is also characterized by process simplicity, short reaction time, easy-to-build equipments, low-energy requirements and the possibility of obtaining complex or metastable phases.

Self-propagating reactions of thermite type, i.e. a metallic or non-metallic oxide is exothermically reduced by a metal to form more stable products [7], have been proposed in the literature to address an important environmental problem, i.e. the fixation of high level radioactive wastes (RAWs) [8]. The proposed process consists of reducing the volume of radioactive liquid wastes and fixing products into a highly insoluble polysilicate structure by means of appropriate thermite reactions. Silicon, iron oxide and silica are used to prepare the thermite mixture and to provide the desired reaction rate and final product composition. Leachability tests and final products were also performed and, although, only the conceptual design of the process has been discussed, the investigation contributes towards the achievement of the permanent fixation of the fission products.

More recently, the exploitation of self-propagating reactions for environmental protection has received renewed attention. In particular, interesting results have been obtained in the following areas: fixation and consolidation of high level RAWs [9], treating and recycling of a highly toxic solid waste from electrolytic zinc plants [10,11], degradation of chlorinated aromatics [12,13] and recycling of silicon sludge

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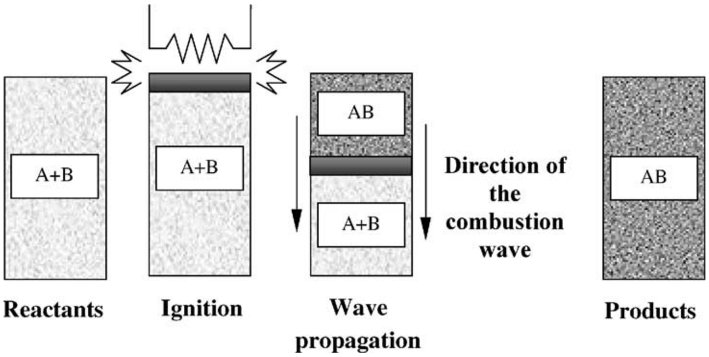

Fig. 1. Schematic representation of SHS process.

and aluminum dross produced by semiconductor industries and aluminum foundries, respectively, [14,15].

The aim of this work is to review the major achievements obtained in these areas. Future scientific and technological directions related to this promising field of reaction engineering are also discussed.

2. Fixation of radioactive wastes

As mentioned in the introduction, the first work available in the literature which takes advantage of self-propagating reactions for environmental applications deals with the fixation of RAWs [8]. The process is based on the use of the following exothermic thermite reaction:

$$4Fe_2O_3 + 3Si \rightarrow 3Fe_2SiO_4 + 2Fe \quad (1)$$

which gives rise to the formation of a polysilicate structure to incorporate the RAWs. The thermite process was preceded by a pre-treatment (evaporation, drying and denitration steps) of the RAWs which was originally in the form of an aqueous solution. Through this treatment all the salts present in the waste solution were converted to oxides. According with reaction (1), the thermite mixture consisted of Si and Fe_2O_3, where silica was sometimes used as additive in order to control the reaction rate as well as the final product composition.

An alternative to the process described above was also proposed by Spector et al. [8]. It differs from the previous in that all salts are in this case converted to sulfates prior to the radioactive element fixation. Accordingly, reaction (1) is in this case replaced by the following one:

$$4Al_2(SO_4)_3 + 9Si \rightarrow 2Al_2O_3 + 9SiO_2 + 6S \quad (2)$$

which provides the polysilicate structure to incorporate the RAWs.

A different process based on combustion reactions to prepare ceramic oxide materials like perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$), hollandite ($Ba_{1.23}Al_{2.46}Ti_{5.54}O_{16}$), and sphene ($CaTiSiO_5$), which can be used for nuclear waste immobilization, has been also proposed in the literature [16]. In fact, these oxides are characterized by the presence of cavities and vacant interlayers in their structures so that they are capable to incorporate radioactive cations ([16] and references therein). Basically, the method involves the wet combustion of metal nitrates, corresponding to the complex oxides to be prepared, together with some fuels, i.e. carbohydrazide (CH_6N_4O), and tetraformyl trisazine ($C_4H_{16}N_6O_2$), at 450 °C, according to the following reactions:

$$7Ca(NO_3)_2 + 7TiO(NO_3)_2 + 5C_4H_{16}N_6O_2 \rightarrow 7CaTiO_3 + 20CO_2 + 40H_2O + 29N_2 \quad (3)$$

$$4Ca(NO_3)_2 + 4Zr(NO_3)_2 + 8TiO(NO_3)_2 + 25CH_6N_4O \rightarrow 4CaZrTi_2O_7 + 25CO_2 + 75H_2O + 70N_2 \quad (4)$$

$$2Ba(NO_3)_2 + 4Al(NO_3)_3 + 9TiO(NO_3)_2 + 21CH_6N_4O \rightarrow \text{Hollandite} + 21CO_2 + 63H_2O + 59N_2 \quad (5)$$

$$2Ca(NO_3)_2 + 29TiO(NO_3)_2 + 2SiO_2 + 5CH_6N_4O \rightarrow 2CaTiSiO_5 + 5CO_2 + 15H_2O + 14N_2 \quad (6)$$

More recently, the direct consolidation of RAWs into perovskite and zirconolite structures using the SHS densification method has been addressed in the literature [9,17].

A mixture constituted by titanium oxide, calcium oxide, zirconium oxide and titanium in powder form, where inactive isotopes of ^{90}Sr and ^{137}Cs are added, was considered to simulate a real composition of radioactive nuclear wastes. By adding calcium nitrate to the mixture above according to the following stoichiometries:

$$2Ca(NO_3)_2 + 9Ti + 4CaO + TiO_2 \rightarrow 6CaTiO_3 + 4TiN \quad (7)$$

$$2Ca(NO_3)_2 + 9Ti + 4CaO + TiO_2 + ZrO_2 \rightarrow 6CaZrTi_2O_7 + 4TiN \quad (8)$$

as well as aluminum and silicon oxide, the resulting green mixture was ignited and simultaneously pressed into suitable moulds. By applying pressure levels up to 200 kg/cm^2, a maximum temperature of about 1500 °C was found during combustion propagation, whose front velocity was in

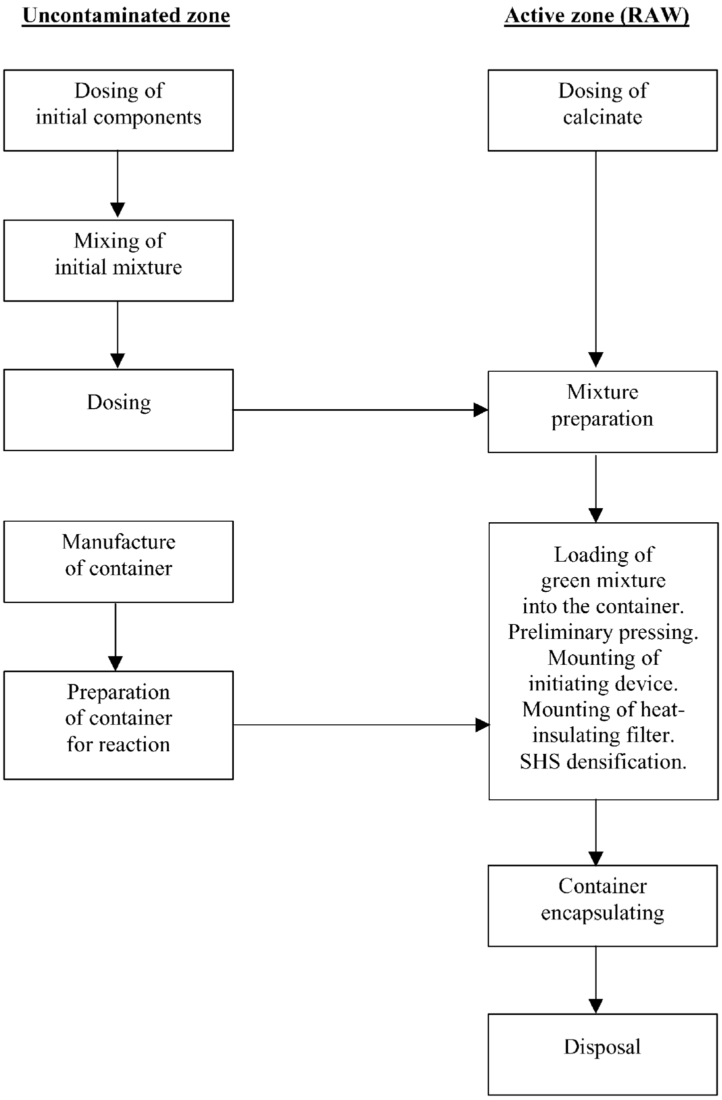

Fig. 2. The technological scheme of RAWs consolidation by SHS [9].

the range of 1–2 mm/s. The density of reaction product was within 3.9–4.2 g/cm^3 while the residual porosity and mechanical strength were found to be <0.2% and about 150 MPa, respectively.

The reaction products display a perovskite structure according with reaction (7) while zirconolite phases are also encountered when zirconium oxide is present in the initial mixture, as expected from reaction (8). It was found that calcium can be isomorphously substituted with strontium in the perovskite lattice. Cesium on the other hand remains entrapped into a non-crystalline phase constituted by silicon and aluminum oxides. Leaching tests of strontium and cesium radionuclides clearly demonstrate that the technique based on the occurrence of self-propagating reactions display a higher chemical stability when compared to standard technologies used for radioactive nuclear waste disposal, i.e. their encapsulation in phosphate and borosilicate glass. A schematic representation of the proposed process for treating radioactive nuclear wastes is reported in Fig. 2.

3. Fixation of toxic species from hydrometallurgical wastes

Highly toxic solid wastes from electrolytic zinc plants, known as jarosite or goethite depending upon the treatment used for iron removal, are currently obtained as by-products (about 750,000 and 90,000 t per year in Europe and Sardinia, Italy, respectively). The large production, the high cost of disposal and the increasing difficulty to find suitable disposal locations, clearly provide a demonstration of their environmental impact [18–20].

Currently, a variety of processing options which provide possible solutions to this acute environmental problem are proposed in the literature. These include hydrometallurgical and pyrometallurgical techniques ([19] and references therein), which are, to some extent, uneconomic or technically risky. On the other hand, glassification, i.e. vitrification of the waste so that hazard components are incorporated into an amorphous glassy structure, is not only an option for environmentally benign disposal but also a promising technique [21]. For example, vitrification in boro-silicate glass is currently used to solidify and stabilize certain forms of radioactive and hazardous wastes. In particular, it has been recently demonstrated that goethite and jarosite waste can be mixed with raw materials and residues such as granite scraps and glass cullet, melted and formed into glass or glass-ceramic matrix which englobes a consistent amount of waste [20]. A preliminary flow sheet of the vitrification pilot plant has been also proposed [22]. The obtained products are currently being characterized in view of the use as construction material.

More recently, Orrù et al. [10] and Sannia et al. [11] have proposed a process of treating and recycling of goethite wastes based upon self-propagating thermite reactions. In particular, taking advantage of the relatively high content of iron oxides in the waste, the following thermite reactions were exploited due to their high exothermic character:

$$2Fe_2O_3 + 3Si \rightarrow 3SiO_2 + 4Fe \tag{9}$$

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \tag{10}$$

$$Fe_2O_3 + 3Mg \rightarrow 3MgO + 2Fe \tag{11}$$

$$Fe_2O_3 + 3Ca \rightarrow 3CaO + 2Fe \tag{12}$$

It was found that by blending this waste with suitable amount of reducing agents (aluminum, silicon, magnesium and calcium) as well as ferric oxide, according to reactions (9)–(12), and igniting the resulting mixture, a combustion wave rapidly travels through the mixture without requiring additional energy, thus converting reactants into two solid products called P_1 and P_2 and a gas mainly containing SO_2. Product P_2 is distributed in powder form in the reaction chamber walls as a consequence of a probable expulsion occurring during the course of the reaction. On the other hand, product P_1 remains in the same position where the original sample was placed inside the reactor. A summary of all mixtures investigated is reported in Table 1.

The occurrence of self-propagating reactions depends upon the combination of reducing agents and the waste content in the starting mixture, as it may be seen from Table 2. The temperature from a thermocouple embedded in the reacting mixture, as described by Orrù et al. [10] and Sannia et al. [11], and the mass ratio of product P_1 with respect to starting mixture are also reported in Table 2. It was found that the combination of aluminum and silicon as reducing agents corresponds to the maximum value of this ratio. In addition, on the basis of the leaching tests performed, the

Table 1
Summary of the mixtures investigated for the treatment of zinc hydrometallurgical wastes by self-propagating reactions [11]

Mixture identification	Waste (wt.%)	Fe_2O_3 from the goethite waste (wt.%)	Fe_2O_3 added (wt.%)	Reducing agent—Al (wt.%)	Reducing agent—Mg (wt.%)	Reducing agent—Si (wt.%)	Reducing agent—Ca (wt.%)	Atmosphere	Sample type
SArP	17.86	7.86	63.36	–	–	18.78	–	Argon	Pellet
AlArP/a	35.71	15.71	44.08	20.21	–	–	–	Argon	Pellet
AlArP/b	44.64	19.64	36.42	18.94	–	–	–	Argon	Pellet
AlArP/c	53.57	23.57	28.75	17.68	–	–	–	Argon	Pellet
MgArP/a	35.71	15.71	39.21	–	25.08	–	–	Argon	Pellet
MgArP/b	44.64	19.64	31.85	–	23.51	–	–	Argon	Pellet
MgArP/c	53.57	23.57	24.49	–	21.94	–	–	Argon	Pellet
MgArP/d	62.50	27.50	17.12	–	20.38	–	–	Argon	Pellet
MgArP/e	71.4	31.43	9.76	–	18.81	–	–	Argon	Pellet
MgArP/f	80.36	35.36	2.40	–	17.24	–	–	Argon	Pellet
CaSAPo	34.48	15.17	39.10	–	–	9.52	16.90	Air	Loose powders
AlSArP/a	35.71	15.71	45.79	10.38	–	8.12	–	Argon	Pellet
AlSArP/b	44.64	19.64	38.01	9.74	–	7.61	–	Argon	Pellet
AlSArP/c	53.57	23.57	30.24	9.09	–	7.10	–	Argon	Pellet
AlSAPo/#	30.00	13.2	50.75	10.81	–	8.44	–	Air	Loose powders
AlSAPo/a	35.71	15.71	45.79	10.38	–	8.12	–	Air	Loose powders
MgSArP/a	35.71	15.71	44.57		9.17	10.55	–	Argon	Pellet
MgSArP/b	44.64	19.64	36.87	–	8.60	9.89	–	Argon	Pellet
MgSArP/c	53.57	23.57	29.17	–	8.03	9.23	–	Argon	Pellet
MgSArP/d	62.50	27.50	21.48	–	7.45	8.57	–	Argon	Pellet
MgSArP/e	71.43	31.43	13.78	–	6.88	7.91	–	Argon	Pellet
MgSAPo/c	53.57	23.57	29.17		8.03	9.23	–	Air	Loose powders
MgAlSArP/c	53.57	23.57	29.68	4.50	4.05	8.20	–	Argon	Pellet

Table 2
Reaction behavior of the reacting mixtures investigated for the treatment of zinc hydrometallurgical wastes by self-propagating reactions [11]

Mixture identification	Self-propagation	Maximum temperature (K)	Mass ratio of P_1 product to starting mixture
SArP	No	–	–
AlArP/a	Yes	2113	0.63
AlArP/b	Yes	2048	0.60
AlArP/c	Yes	2026	0.67
MgArP/a	Yes	2849	0.83
MgArP/b	Yes	2791	0.75
MgArP/c	Yes	1855	0.70
MgArP/d	Yes	1844	0.68
MgArP/e	Yes	1617	0.68
MgArP/f	No	–	–
CaSAPo	Yes	–	–
AlSArP/a	Yes	1794	0.85
AlSArP/b	Yes	1706	0.84
AlSArP/c	No	–	–
AlSAPo/#	Yes	–	–
AlSAPo/a	Yes	–	–
MgSArP/a	Yes	1735	0.79
MgSArP/b	Yes	1681	0.77
MgSArP/c	Yes	1710	0.77
MgSArP/d	Yes	1409	0.76
MgSArP/e	No	–	–
MgSAPo/c	Yes	–	–
MgAlSArP/c	Yes	1565	0.75

corresponding product P_1 was found to fulfill the very restrictive environmental regulations for heavy metals. This result was justified by the microstructural characterization of product P_1 obtained using the combination Al/Si as reductants. In fact, for the case of AlSArP/a mixture, it may be seen from Figs. 3a and 4 that product P_1 is constituted by an amorphous glassy structure of iron alumino-silicates embodying heavy metals. A process for the treatment of zinc hydrometallurgical wastes, for which a schematic representation is shown in Fig. 5, has been proposed. It may be seen that the solid product P_2, whose XRD analysis corresponding to the AlSArP/a mixture is also reported in Fig. 3b, may be recycled in the roasting unit of the industrial zinc production plant, due to its composition. It should be noted that although commercial iron oxide, aluminum and silicon have been used the possibility of taking advantage of the corresponding waste analogue is currently being investigated.

4. Degradation of chlorinated aromatics

The destruction of health threatening compounds has become one of crucial problem in the area of hazardous waste management [23]. Organo-chlorine pesticides, polychloric biphenyls, dibenzofurans, dioxins and other synthetically produced derivatives of chlorobenzene are some of the common and most politicized substances that must be dealt with. Indeed, aromatic rings with halogen substitution are highly resistant to oxidative degradation and the possible emission of even worse by-products appears one of the main disadvantages of conventional incinerator technologies.

Recently, the attention has been directed to the exploitation of self-propagating reactions to degrade chlorinated aromatics [12,13]. Hexachlorobenzene (C_6Cl_6) and the racemate of 2-(2,4-dichlorophenoxy)-propanoic acid ($C_9H_8Cl_2O_3$), a commercial herbicide known as dichloroprop-hereafter 2,4-DP, were used as chlorinated test species, while calcium hydride was proposed as reducing agent. Reactants were first mixed according to the following reactions:

$$3CaH_2 + C_6Cl_6 \rightarrow 3CaCl_2 + 6C + 3H_2 \quad (13)$$

$$6CaH_2 + C_6Cl_6 \rightarrow 6CaHCl + 6C + 3H_2 \quad (14)$$

$$4CaH_2 + C_9H_8Cl_2O_3 \rightarrow 3CaO + CaCl_2 + 9C + 8H_2 \quad (15)$$

$$5CaH_2 + C_9H_8Cl_2O_3 \rightarrow 3CaO + 2CaHCl + 9C + 8H_2 \quad (16)$$

The resulting mixtures were then pressed into cylindrical pellets and fitted into the sample holder of the reaction chamber. The reaction was run under a slight overpressure of purified argon. Samples were fired by a power pulse (2 s) of about 2 kW by means of a tungsten coil. After the thermal

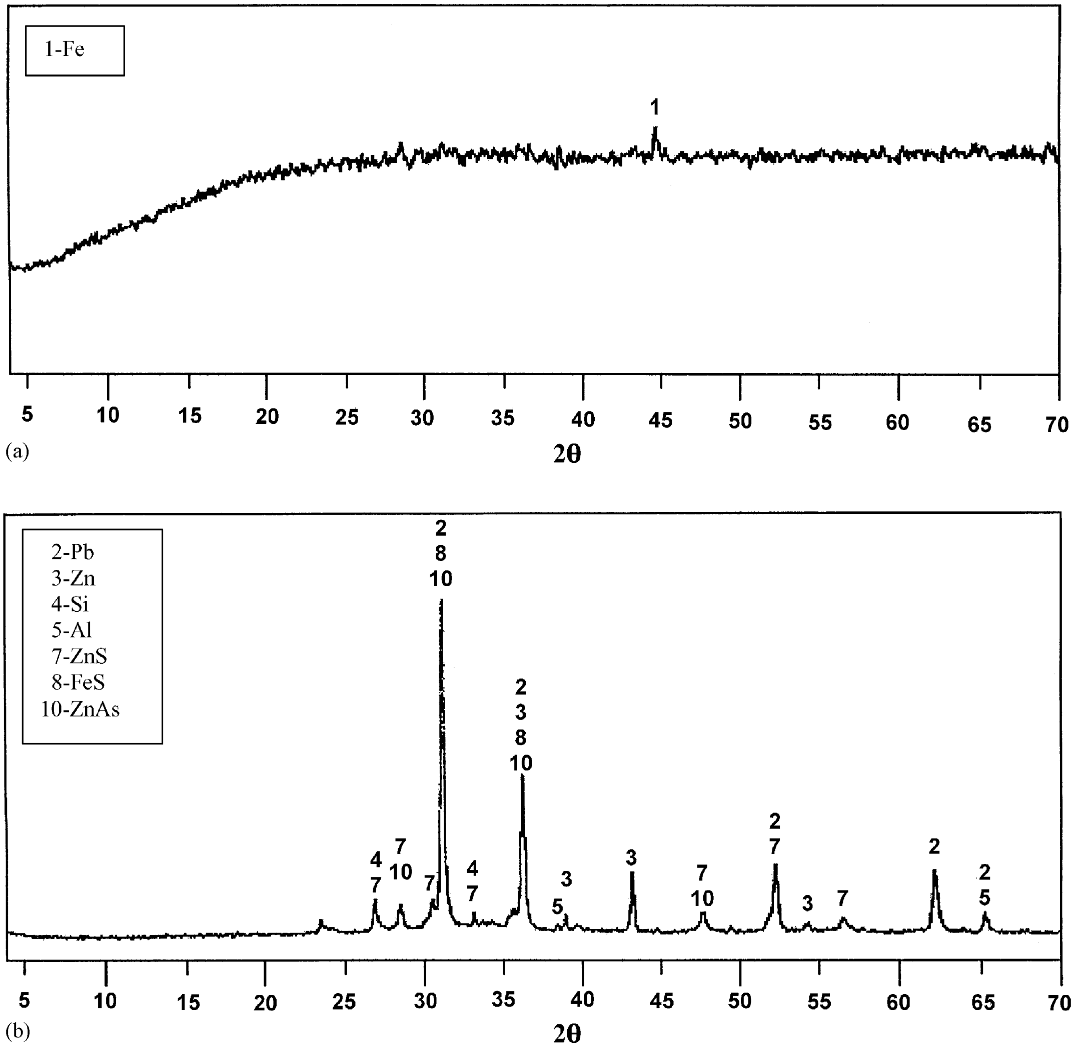

Fig. 3. CuKα XRD spectra of product: (a) P_1 and (b) P_2 obtained when reacting AlSArP/a sample during the treatment of zinc hydrometallurgical wastes [10].

spike, the reaction spreads spontaneously through the whole sample.

These features reflect the highly exothermic qualities of the reactions involved. From reference data, a reaction enthalpy of 1709.6 kJ/mol is foreseen for the direct and complete reduction of hexachlorobenzene represented by reaction (3), which rises to 1804.6 kJ/mol when an excess of CaH_2 is employed. In the case of 2,4-DP, reaction enthalpies of −1295.4 kJ/mol and −1321.7 kJ/mol for reaction (15) and (16), respectively, were calculated [24].

The reaction heats above are large enough to maintain the self-sustaining character of the process within a wide range of compositions. Indeed the combustive regions are similar for the two test compounds, and extend from a CaH_2/organo-halide molar ratio of about 2–3 up to 15–18, i.e. up to a very large excess of calcium hydride. The maximum temperature of the propagating reaction front was observed in the stoichiometric ranges given by reactions (1)–(4). For example, a combustion temperature above 2650 K was registered using an infrared pyrometer for a CaH_2/C_6Cl_6 mixture with a molar ratio of 3. This value is similar to the calculated adiabatic temperature of 2984 K. The reaction temperature progressively decreased with increasing the CaH_2 content in the mixture. This is due to the excess of CaH_2 which does not contribute to the reaction heat, while increasing the total heat capacity of the system. It was found that the reaction propagation rate obtained from video-records for the whole range of examined compositions was to be between 0.5–1.5 cm/s.

According to the straightforward pathways proposed in reactions (13)–(16), relatively low CaH_2/organo-halide benchmark ratios are demanded for the complete reduction of the chloro-organics. At least 3 mol of calcium hydride are required in the case of hexachlorobenzene and four or five in the case of 2,4-DP. Samples from the reactor's head space were analyzed by gas chromatography/mass spectroscopy (GC/MS). Hydrogen and methane (with CO and CO_2 in the case of 2,4-DP) were the main gaseous compounds

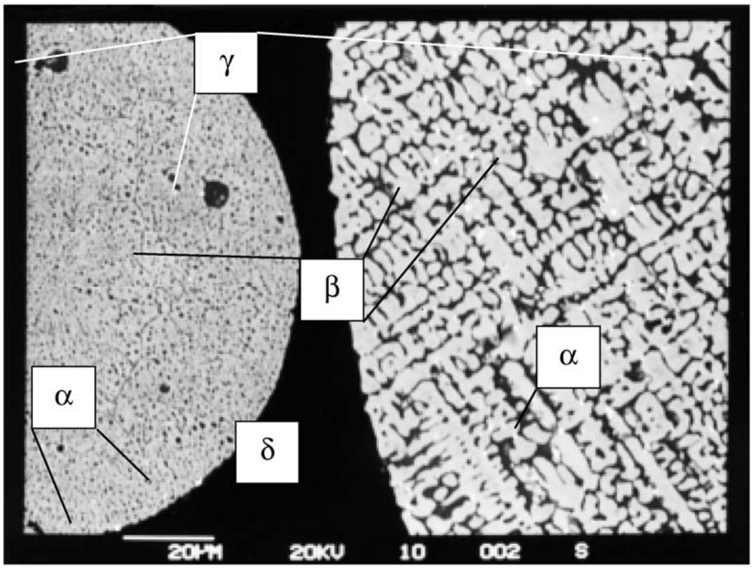

Fig. 4. SEM back-scattered view of the microstructure of the product P_1 obtained when reacting AlSArP/a sample: (α) lead, (β) iron, (γ) iron sulfide, (δ) iron alumino-silicates [10].

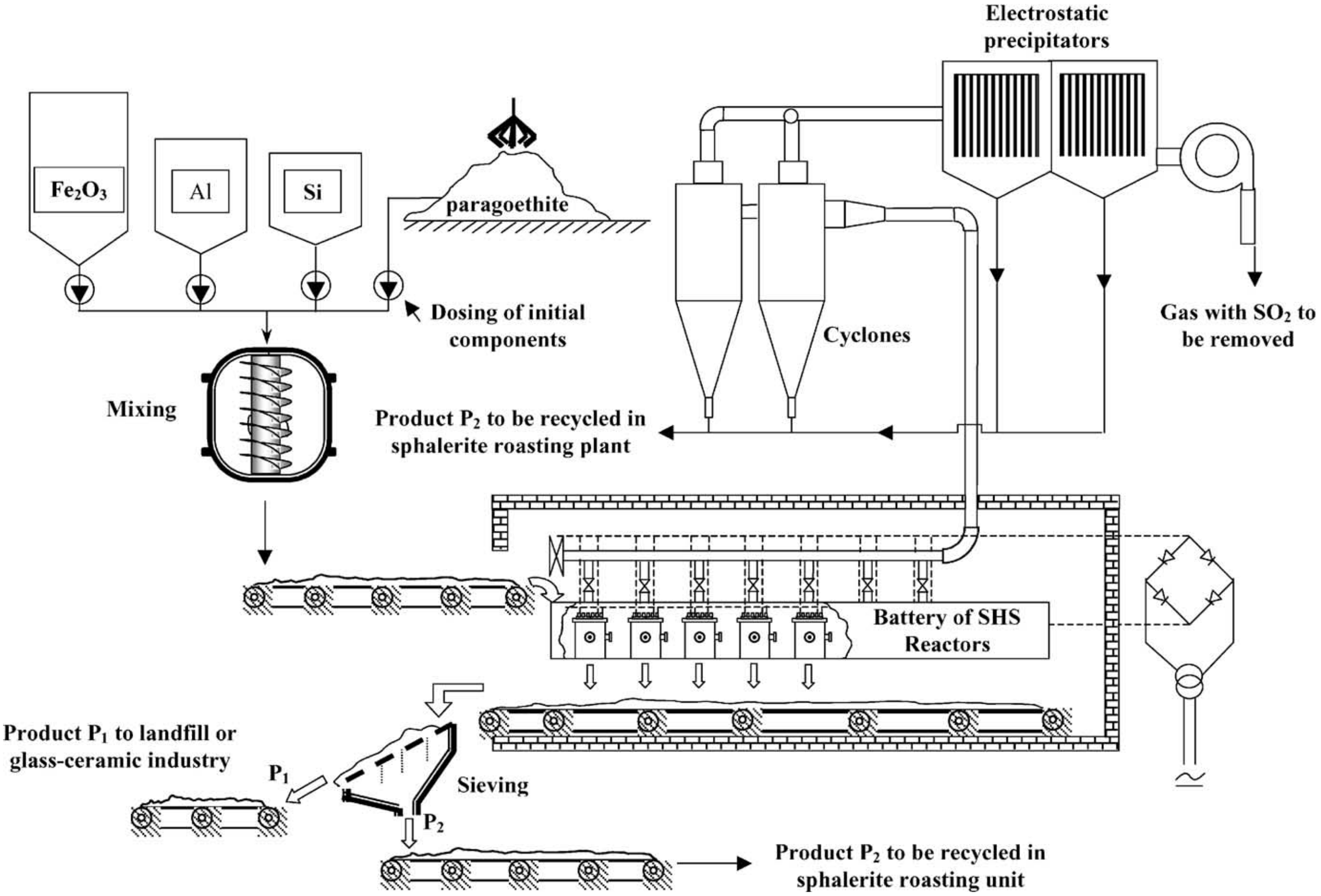

Fig. 5. Schematic representation of the proposed process for treating and recycling of goethite waste [11].

[12]. Traces of benzene, mono-, di- and tri-chlorobenzene, dichloroethylene, dichloro-methane, xylene and trimethylbenzene were also found by utilizing environmental protection agency (EPA) method TO15 [12]. Organic solid end-products in the reacted powders were also analyzed by high resolution GC/MS. We found consistent concentrations of reaction products, the total organo-chlorine conversion resulting in each trial is >99.999%.

As shown in Fig. 6, the transformation of reactants into non-toxic low-energy was also confirmed by the X-ray analysis. In the case of hexachlorobenzene (cf. Fig. 6a), the burnt powders were found to consist of graphite, $CaCl_2$ and CaHCl, the hydride–chloride mixed salt becoming the predominant phase at the larger CaH_2 content. In the case of 2,4-DP (cf. Fig. 6b), CaO was also found. These preliminary results suggest that self-activating processes can be an alternative to conventional thermal treatments of hazardous chlorinated aromatics. The advantages are obvious in that very high temperatures are locally reached with low pressure and under extent-controlled conditions. Solid and gaseous reaction products can be easily checked before their discharge. The simplicity and a very low-energy requirement are two other merits of the process.

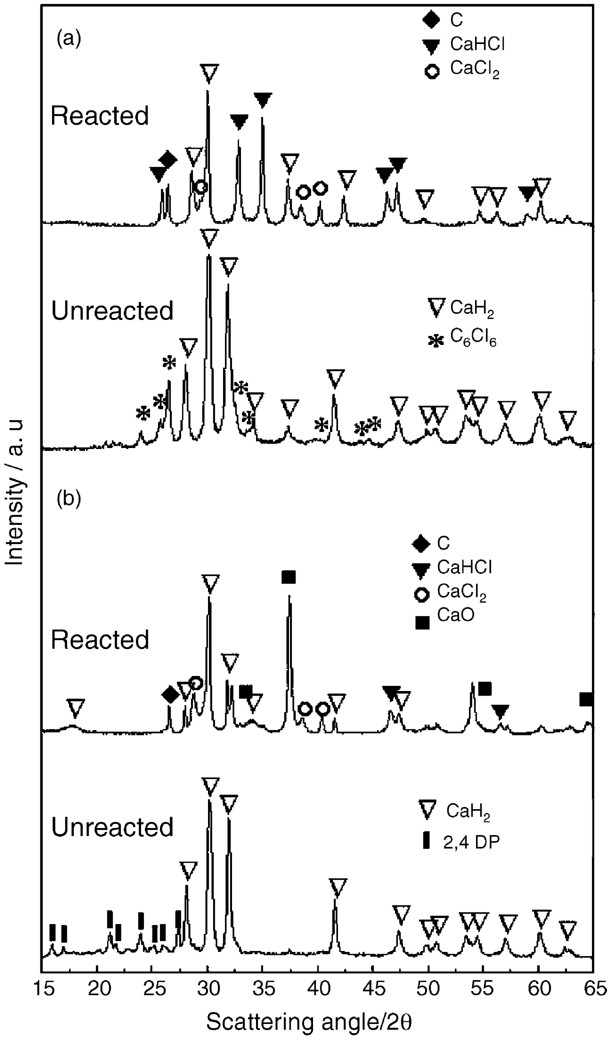

Fig. 6. CuKα XRD patterns of the burnt powders for: (a) CaH_2-C_6Cl_6 mixture with a molar ratio of 12 and (b) CaH_2-2,4-DP with molar ratio of 12. The patterns of the as-prepared mixtures are also reported. The angular positions of the main peaks are shown according to the JCPDS file quoted in the inset [13].

It should be noted that relatively simple facilities are required by large scale SHS production up to 100 t per year. However, the practical exploitation of the presented methodology for large scale waste treatment requires further investigation.

5. SHS recycling

In addition to the application of self-propagating reactions described above and following previous studies related to silicon wastes in zinc smelting [25], a new recycling process based on the SHS nitriding combustion of silicon sludge from semiconductor industries and aluminum dross from aluminum foundries both to obtain silicon based ceramics has been proposed [14,15].

The process treatment of silicon sludge is based on the combination of silicon with nitrogen to form Si_3N_4 according to the following exothermic reaction:

$$3Si + 2N_2 \rightarrow Si_3N_4 \qquad (17)$$

which is characterized by a reaction enthalpy of 748 kJ/mol and an adiabatic temperature of 4127 °C [25]. However, since the composition of the silicon sludge is Si (26 wt.%), Al_2O_3 (14 wt.%), $ZrSiO_4$ (31 wt.%), Fe_2O_3 (27 wt.%) and CaO (2 wt.%), the silicon content is too low to make the nitridation of the sludge possible by SHS. To overcome this problem, reclaimed Si and Al powders produced by silicon and aluminum industries, respectively, were added to the waste.

The resulting mixture is then ignited by passing a current of 50 A for 5 s through a carbon ribbon heater in a pressurized nitrogen atmosphere until a self-propagating reaction takes place. The product consisted of three different sialon compositions (i.e. $Si_6Al_{10}O_{21}N_4$, $Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}$ and $Si_3Al_3O_3N_5$), iron silicides ($FeSi_2$) and monoclinic zirconia (ZrO_2). The mechanical and thermal properties of the obtained sintered compacts are reported in Table 3(A).

With the aim of improving the oxidation resistance, the iron oxide in the silicon sludge was eliminated by leaching it with hydrochloric acid. With this treatment, calcium oxide was also removed from the sludge, whose resulting composition became Si (31 wt.%), Al_2O_3 (30 wt.%), $ZrSiO_4$ (35 wt.%). In this case the product consisted of sialon (80 wt.%) and zirconia (20 wt.%). It was sintered 1600 °C for 2 h and the mechanical and thermal properties of the resulting compact are listed in Table 3 (B). It is interesting to note that the product strength is lower than conventional sialon (about 360 MPa) but may be compared with silicon nitride obtained by reactive sintering (about 250 MPa).

Table 3
Mechanical and thermal properties of the sintered compacts obtained during the recycling process of silicon wastes by SHS [14,15]

	Bulk density (g/cm^3)	Bending strength (MPa)	Thermal expansion coefficient (10^{-6}/K)	Weight change (1200 °C/10 h) (mg/cm^2)	
				Ar	Air
A	2.7	150	4.8	−1.9	+7.2
B	3.0	270	4.5	−0.7	+0.25

The other SHS recycling process proposed in the literature which makes use of aluminum dross is based on the nitridation of aluminum according with the following reaction:

$$2\mathrm{Al} + \mathrm{N}_2 \rightarrow 2\mathrm{AlN} \quad (18)$$

characterized by a combustion heat of 11855 kJ/kg [15]. Aluminum dross, whose composition was 75 wt.% AlN, 12.5 wt.% Al_2O_3 and 12.5 wt.% Al, was first pulverized and mixed with reclaimed silicon to make the self-propagation combustion possible, following a procedure similar to the one described above. The resulting mixture was then combusted under nitrogen atmosphere and the resulting product consisted of $Si_{6-x}Al_xO_xN_{8-x}$ and other Si–Al–O–N phases.

Thus, by taking into account the large world-wide production of silicon wastes from semiconductor industries and aluminum dross, the proposed recycling process based on the exploitation of self-propagating reactions appears to be a promising alternative to the non-productive disposal of these wastes.

6. Discussion and future scientific-technological directions

In the first part of this work, the major achievements in the field of self-propagating reactions exploited for environmental protection have been reviewed. It is shown that the applicability of this strategy of waste inertization, minimization and reuse clearly depend upon the availability at relatively low cost of suitable reducing agents. This aspect may represents the main drawback of the proposed technologies based on self-propagating reactions. In fact, although reducing agents as scraps may be potentially available on the market, the use of the corresponding commercial products is often mandatory to overcome their unavailability. On the contrary, the exploitation of self-propagating reactions allows one to take advantage of the classical features of the technologies based on this type of reactions and used to synthesize a wide variety of advanced materials [6], i.e. short synthesis times, process simplicity, low-energy requirements, etc. [26].

It should be noted that the potential merit of SHS, i.e. the low process costs outlined above, tends to be canceled in many applications of materials synthesis by high cost of initial components such Ti, Mo, B, etc. to produce titanium carbide, molybdenum silicides, borides, etc. On the contrary, they may be fully utilized when ecological applications of self-propagating reactions are taken into account.

The practical exploitation of the SHS technology for environmental protection, may be also improved through a deeper understanding of kinetics and mechanism of solid–solid and gas–solid self-propagating reactions. This represents a very complicated task, as recently pointed out in the literature [6], due to the unique aspects of complex physico-chemical phenomena simultaneously taking place (melting and diffusion of reactants, chemical reactions with formation of intermediate phases, nucleation, grain growth, etc.). In fact, it should be noted that only few techniques are available to perform SHS kinetics and mechanistic studies, i.e. time resolved XRD analysis, particle-foil experiments and combustion front quenching, which allow to identify reactions and phase transformations taking place. Unfortunately, these investigation techniques are often characterized by difficulties in the experiments and their interpretation, even for systems constituted by two reactants. The complex nature of the systems investigated in the light of exploiting self-propagating reactions for environmental protection, clearly prevent a comprehensive study of the corresponding kinetics and mechanisms of structure formation taking place. This difficulty is also enhanced by the limitation of experimental techniques discussed above. However, it should be noted that studies of this type, where the main goal is to establish direct and reciprocal relationships between the combustion conditions and structure formation are known in the literature as structural macrokinetics investigations and represent one of the most promising research directions for the future exploitation of solid–solid and gas–solid self-propagating reactions.

Along these lines, the comparison between thermally and mechanically activated self-sustaining reactions may provide new insights and possible lines of inquire may emerge. For the case of hexachlorobenzene degradation, according to reactions (13) and (14), a comparison between these two processes which run under quite different regimes has been recently presented [12]. In particular, a well defined activation barrier exists for the occurrence of a self-propagating thermal wave, while mechanochemical reactions are initiated under the conditions of continuous defect generation and progressive structural instabilities ([27], and references therein). Despite these features, it is shown that the same underlying mechanism seems operative in both processes as suggested by the close correspondence in the whole combustion range, between the temperature and the propagation wave velocity and the values representing the instantaneous temperature reached in the milled powders at the spontaneous propagation stage. The same combustion products, found at the end of the reactions [12], confirm the similarity of the chemical transformations involved. A very promising research direction is to extend this strategy of investigation to other systems in order to highlight the mechanism involved during self-propagating reactions for environmental protection as well as other interesting application in the field of materials science and technology [28,29].

In addition to the consideration above, the design of reactors for self-propagating reactions represents a very complex reactor problem, as pointed out by Hlavacek et al. [5,30]. This is mainly due to the rich spectrum of phenomena associated to solid–solid and gas–solid self-propagating reactions, such as the explosive expulsion of gases during reaction evolution, the melting of intermediate or final products, etc. which typically requires the design of a specific reactor. These aspects are of great importance when developing suitable technologies based on self-propagating reactions for residues recycling and environmental waste disposal. In addition, the availability of large-scale processes based on this technique should be taken into account due to the intensive production of wastes world-wide. While up to 1000 t of material output may be handled by taking advantage of batteries of batch reactors, a very important technological challenge is represented by the development of continuous reactors where self-propagating reactions of solid–solid or gas–solid type take place [31]. Along these lines, a screw and roll reactor have been suggested recently [31]. In the first case, reactants are loaded into the reactor through a screw and subsequently reacted in a nozzle where the position of the combustion front is stabilized. Simultaneously, the products may be powdered in a rotor mill. The roll reactor consists of two rotating rolls through which the obtained products are conveyed. However, practical exploitation of these continuous reactors seems to be very difficult for several reasons. Firstly, some operational problems may arise from the movement of the reacting mixture inside the reactor, since hard solid materials may cause strong erosion of the reactor tube. Moreover, reacting media can have the tendency to sinter which may stop the flow. The same problems may result if gas evolution occurs during the reacting process. All these inconveniences make the stabilization of the front difficult, which is, on the other hand, a necessary requirement for handling continuous reactors based on this technology. Thus, beside some confidential reports available at this stage, the development of continuous reactors where self-propagating reactions occur may be considered still in its infancy.

Finally, it is worth mentioning that, apart from the technology reviewed in this paper, comparisons of different existing processes for residues recycling and waste disposal have to be performed to evaluate the most appropriate choice.

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