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Simultaneous solidification of two catalyst wastes and their effect on the early stages of cement hydration

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Abstract Two catalyst wastes (RNi and RAI) from polyol production were considered as hazardous, due to their respective high concentration of nickel and aluminum contents. This article presents the study, done to avoid environmental impacts, of the simultaneous solidification/stabilization of both catalyst wastes with type II Portland cement (CP) by non-conventional differential thermal analysis (NCDTA). This technique allows one to monitor the initial stages of cement hydration to evaluate the accelerating and/or retarding effects on the process due to the presence of the wastes and to identify the steps where the changes occur. Pastes with water/cement ratio equal to 0.5 were prepared, into which different amounts of each waste were added. NCDTA has the same basic principle of Differential Thermal Analysis (DTA), but differs in the fact that there is no external heating or cooling system as in the case of DTA. The thermal effects of the cement paste hydration with and without waste presence were evaluated from the energy released during the process in real time by acquiring the temperature data of the sample and reference using thermistors with 0.03 °C resolution, coupled to an analog–digital interface. In the early stages of cement hydration retarding and accelerating effects occur, respectively due to RNi and RAl presence, with significant thermal effects. During the simultaneous use of the two waste catalysts for their stabilization process by solidification in cement, there is a synergic resulting effect, which allows better hydration operating conditions than when each waste is solidified separately. Thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) of 4 and 24 h pastes allow a quantitative information about the main cement hydrated phases and confirm the same accelerating or retarding effects due to the presence of wastes indicated from respective NCDTA curves.

Keywords Waste catalysts · Solidification · Stabilization · Cement · NCDTA · TG

Introduction

The generation of a certain amount of by-products and waste always occurs in production and consumption systems. Taking into account the nature, location and the generated quantities, the wastes can present several problems involving social, economic, political, environmental, and health issues. One of the main challenges for Brazilian industries has been the management of their industrial waste in accordance to environmental law requirements.

Solidification and Stabilization (S/E) is one of the many ways of industrial wastes treatment. The process of S/E based on cement has been used for industrial wastes containing heavy metals, such as cadmium, chromium, copper, lead, nickel, and zinc [1–4]. This technique seeks the immobilization of hazardous wastes, using the properties of cement hydration [5]. The mechanism used for S/E and the evaluation of its effectiveness has been widely studied and discussed [6, 7].

The cement hydration process starts immediately after its contact with water, when it begins the formation of

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hydrated phases and the dissolution of ionic species in liquid phase, completing this process in about 28 days. The control of cement hydration depends on the knowledge of the variables that determine the kinetics of the involved reactions [8, 9].

The addition of industrial wastes and additives can change the S/E process [4]. By micro-spectroscopy it can be seen that Co and Ni react differently during the cement hydration and both are immobilized in cement matrix [10]. Several studies on S/E of residues in cement matrices show that contaminants interfere with the hydration reactions by retarding or accelerating the solidification of the cement paste [11, 12]. Poon et al. [13, 14] reported that metals that form soluble hydroxides behave as accelerators of hydration reactions and metals that form the least soluble hydroxides retard cement hydration. "Retardation has been attributed to the impermeability reduction caused by these reaction products, that is, the precipitation of insoluble metal colloidal gels on cement grain surfaces" [1].

Thermal analysis has been used to evaluate cement hydration processes. The exothermic effects that occur during the early stages of cement hydration can be measured by adiabatic, semi-adiabatic, isothermal, isoperibolic, differential and conduction calorimetry, and NCDTA [15–19]. All these techniques result on very similar curves, which show the instantaneous heat flux and accumulated flux or values directly proportional to them (in NCDTA case) as a function of time. They are mainly used to directly analyze accelerating or retarding effects of operating parameters on mainly cement pre-induction and acceleration cement hydration stages, which are characterized by respective curve peaks. Pacewska et al. [20] report from differential calorimetry curves that the "addition of fly ash extends the induction period as well as shifts the second heat effect" (of the acceleration stage), when compared to the cement paste without ash. Winnefeld et al. [9] show, from isothermal conduction calorimetry data, that the formation of calcium sulfoaluminate in the early hydration stages can be accelerated by addition of calcium sulfate. Lou et al. [21] state that "the accelerating effect of Portland limestone cement on hydration is clearly visualized by the isothermal calorimetric analyses." Kadri et al. [22] conclude that "semi-adiabatic calorimetry have shown that the addition of silica fume in concrete alters the hydration process at very early ages." Using only NCDTA results, Cherem da Cunha et al. [23] studied the effect of metakaolin pozzolanic activity and Pinto et al. [24] the influence of the presence of runoff storm water runoff residuals, in both cases, on the early cement hydration stages.

In this article is shown a S/S study of two catalyst wastes from polyols production in Rio de Janeiro State, Brazil, considered as hazardous by local environment regulation [25] due to their respectively high concentration of Nickel and Aluminum. The effects on the process due to their simultaneous presence during the initial stages of cement hydration were evaluated, as well as the steps where the changes occur.

Materials and methods

Commercial Portland cement (CP) type II, code CPII-F32, (manufactured by Lafarge, RJ, Brazil) was used for the S/E of the catalyst wastes containing Nickel (RNi) and Aluminum (RAl).

In order to study the thermal effects of the wastes addition in cement paste by non-conventional DTA (NCDTA), cement pastes with water/cement ratio equal to 0.5 were used. The samples were composed always by 100 g of cement adding different quantities of catalyst wastes. According to Dweck et al. [26], the use of 100 g of cement allows good operating conditions to study its hydration. According to Glasser [27], in the process of hydration of cement, the water/cement ratio is an important factor to be considered: ratios below 0.25 are insufficient to enable all the hydration reaction. However, ratios of water/cement greater than 0.35 increase the fluidity and the porosity, obtaining as a result, higher permeability and lower resistance.

Regarding the content of the simultaneous use of the two catalyst wastes, in a first set of samples 30 mass% addition of RNi was fixed, changing the added quantities of RAl (5, 10, 15, 20, and 30 mass%) and in a second group of samples, 30 mass% of RAl was fixed, changing the amounts of added RNi (5, 10, 15, 20, and 30 mass%). Samples with separately added RAl and RNi catalyst wastes were also studied, with 5, 10, 15, 20, and 30 mass% of waste added to cement paste. We used the maximum value of 30 mass% addition because previous leaching studies showed this limit as acceptable, regarding the final environmental stability needed for nickel and aluminum and to have a good workability as well [28, 29]. Leaching tests [30] done for all the compositions studied in this article presented acceptable values for the final concentrations of Ni and Al in the leaching extracts, with maximum respective values of 0.2 and 1.8 mg L^{-1} for the sample using the addition of the highest amount of the two catalyst wastes (30 mass% RNi + 30 mass% RAl). As there are no explicit values in Brazilian environmental laws for the acceptable limits for Ni and Al contents for leaching tests, the Australian governmental respective limits of 2 and 5 mg L^{-1} were taken as the acceptable ones [31].

In order to study the early stages of hydration, a NCDTA system was used which has the same basic principle of Differential Thermal Analysis (DTA), but differs in the fact that there is no external heating or cooling system as in the case of DTA [26]. The method allows the study of the effects of thermal evolution of the cement pastes hydration with and without waste addition at ambient temperature, as well as to evaluate the released energy that occurs during the process. The measurements are done in real time by acquiring the temperature data of the sample and reference through thermistors with 0.03 °C resolution, coupled to an analog–digital interface from Vernier LabPro TM, during NCDTA analysis. The difference between sample and reference temperatures ($T_s - T_r$) is generated by the exothermic effects of cement paste hydration reactions, which is directly proportional to the generated heat flow as a function of time. This technique is very effective to evaluate the main effects of the presence of the wastes on cement hydration during the early S/E process [18, 32, 33]. More details of the measuring system can be found in previous articles [26]. As shown in Fig. 1, the interface measures the sample and inert reference temperatures (T_s and T_r) and micro processes the data through a computer. The inert reference consists of a previously solidified cement paste for more than 28 days of hydration. The samples were prepared into polystyrene cups, mixing the respective amounts of waste and water and adding afterward the cement. There are actually four simultaneous measuring devices (one for the reference and three for samples), with respective thermistors inserted into the reacting samples as shown in the detail of Fig. 1. The polystyrene cups are inserted in respective Styrofoam vessels to isolate them thermally from ambient. A lid, through which the thermistors are inserted, seals the intern ambient of the cups. A control sample (CPII) with 100 g of cement and 50 g of water was also analyzed.

Chemical analysis of the cement and catalyst wastes was performed by X-ray fluorescence, by compacted powder method in a Rigaku, KIX: 3100 equipment with Rh tube. The catalysts wastes were also analyzed by X-ray diffraction using a Rigaku MiniflexII diffractometer, the radiation was Kα of copper of 1.542 A, with steps of 0.050° (2θ) every second.

TG and DTG of the raw materials and of the same samples analyzed by NCDTA were performed in a simultaneous TA Instruments TG–DTA equipment, model SDT 2960, with a 10 °C $\min^{-1}$ constant heating rate, from 30 to 1000 °C, in 100 mL air flow. Samples of about 10 mg were used in open platinum pans. Unless differently stated, all hydrated paste samples were initially dried at 35 °C for 1 h in the equipment, before the constant heating rate step was initiated.

Results and discussion

The chemical compositions of cement (CP) and catalyst wastes (RNi and RAl) are shown in Table 1. X-ray diffraction patterns of catalyst wastes are shown in Figs. 2 and 3. XRD data of RAl show the presence of B-Bayerite; G-Gibbsite and N-Nordstrandite ($Al(OH)_3$) and H–Halite (NaCl). RAl consists mainly of aluminum hydroxide polymorphs and sodium chloride, which are formed in the different steps of the industrial process. For RNi catalyst waste, XRD data show the presence of SC-Sodium Chloride (NaCl); CC-Calcium Carbonate ($CaCO_3$); SS-Sodium Aluminum Silicate Hydroxide ($NaAl_2(AlSi_3O_{10})(OH)_2$); SA-Sodium Aluminum Hydrate ($NaAl(OH)_4$); NO-Nickel Oxide (NiO) and NS-Nickel Silicate (Ni_2SiO_4). Thus, RNi waste is a more complex waste than RAl. According to Scheidegger et al. [34, 35], previous experiments with Ni compounds indicate that in an alkaline environment like a cement matrix (pH 12.5) poorly crystalline $Ni(OH)_2$ phases are formed, which is probably the cause why it did not appeared in RNi XRD pattern.

The cement hydration process is exothermic with a significant temperature increase in the early stages. Figures 4 and 5 show the NCDTA curves of the pastes with separate use of residues, compared to the cement paste control sample without addition of waste. The first peak of each

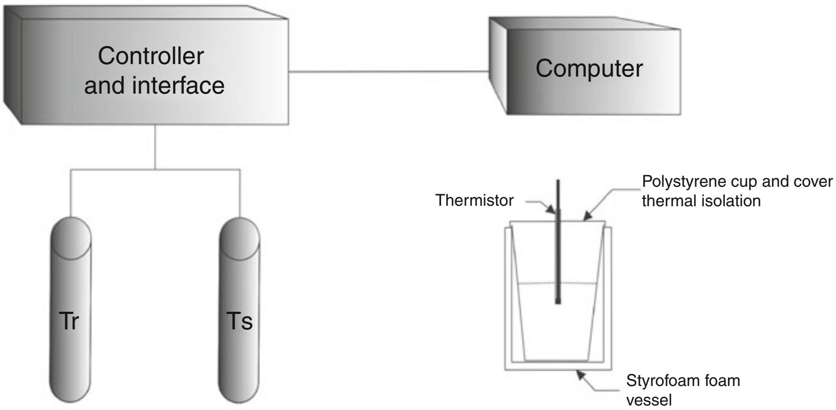

Fig. 1 Simplified schematics of the NCDTA system

Table 1 Chemical composition of Portland cement and catalyst wastes (RNi and RAl) dried at 60 °C (in mass%)

Compounds	Portland cement (CP)[a]	Residual waste (RNi)	Residual waste (RAl)
Al_2O_3	3.70	7.505	70.221
Na_2O	0.070	n.d.	14.425
Cl	n.d.	8.168	10.023
SiO_2	19.98	12.918	3.246
SO_3	n.d.	1.743	1.819
K_2O	0.80	0.833	0.164
CaO	62.80	39.507	0.039
NiO	n.d.	28.316	n.d.
Fe_2O_3	3.12	0.93	n.d.
MgO	3.10	n.d.	n.d.

n.d. not determined

[a] Supplied by the manufacturer

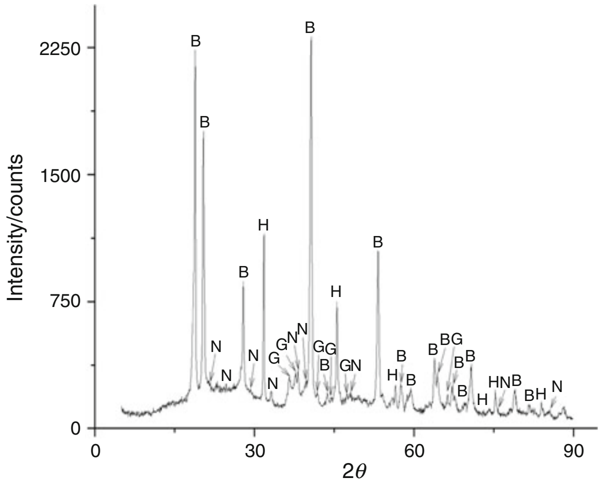

Fig. 2 XRD pattern of the RAl catalyst waste

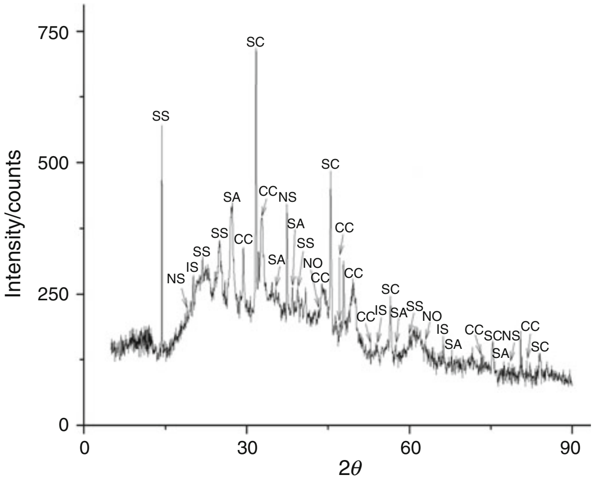

Fig. 3 XRD pattern of RNi catalyst waste

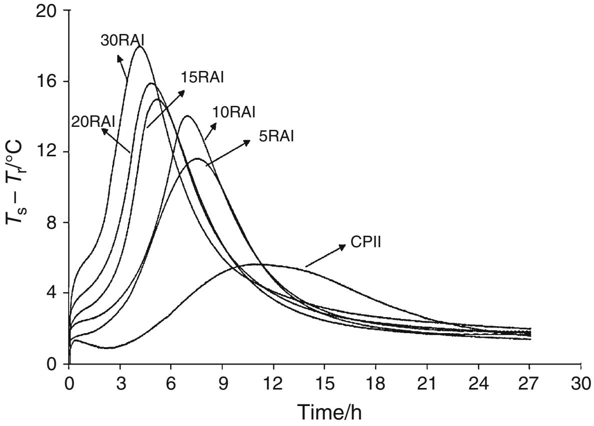

Fig. 4 NCDTA curves of pastes with only RAl addition and control paste

curve, which occurs during the first hours of reaction, is characteristic of tricalcium aluminate (C_3A) hydration in gypsum presence forming ettringuite ($CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 32H_2O$). During the hydration process, this stage is known as pre-induction period, followed by the induction period with a very low heat evolution [26]. The second and higher NCDTA peak is due to tricalcium silicate (C_3S) hydration, forming tobermorite ($3CaO \cdot 2SiO_2 \cdot xH_2O$) and calcium hydroxide ($Ca(OH)_2$) [26, 36]. This stage, called acceleration period, is characterized by an increase in the hydration rate until a maximum value of sample and reference temperature difference occurs.

In the analyses performed with the use of each residue, it was found that the addition of the aluminum-containing waste in cement paste reduced or practically eliminated the induction period, accelerating significantly the hydration reactions of the acceleration period (Fig. 4), while adding nickel-containing residue retards them, extending the duration of induction period, (Fig. 5) and these effects are clearly observed from the time when the accelerating period begins and from the time when occurs the maximum

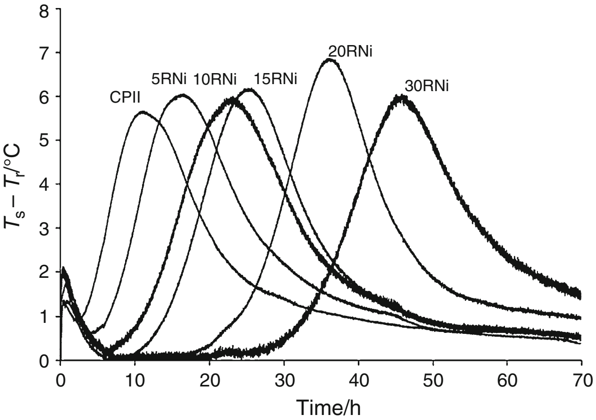

Fig. 5 NCDTA curves of pastes with only RNi addition and control paste

of the second NCDTA peak. In Fig. 4, with all samples with addition of RAl, maximum peaks occur before the maximum peak of the cement control paste (about 12 h), indicating that an accelerating effect occurs at early hydration times (less than 1 day). The opposite behavior was observed with the group of RNi pastes, as shown in Fig. 5, with all samples presenting the second NCDTA peak after the occurrence of the correspondent peak of CPII control sample. Even using a sample with 5 mass% of RNi addition it was possible to notice that there was a retarding effect on cement hydration of about 5 h when compared with the control paste case. As can be seen from Fig. 6, the retarding effect of RNi waste is practically a linear function of its added content, whereas the accelerating effect of RAl waste decreases non linearly, as its added content increases. It must be noted that as done in the present article, many other studies have concluded about the accelerating or retarding effects on cement hydration, from the duration and time of occurrence of the early stages of hydration from these main peaks of calorimetric curves.

The NCDTA curves of the pastes prepared with the simultaneous use of the two catalyst wastes are shown in Figs. 7 and 8, from which it can be seen that the concentration of the wastes influences the solidification process, retarding or accelerating the early stages of cement hydration and that such thermal effects on pastes containing wastes are significant.

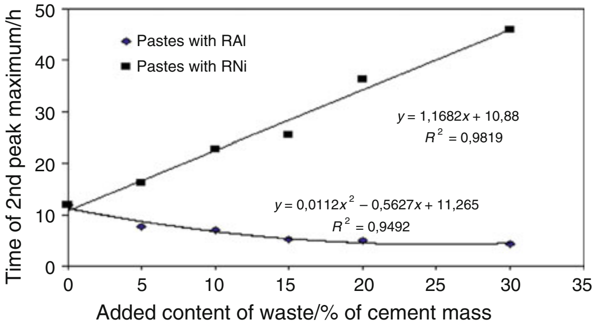

Fig. 6 Time of occurrence of the NCDTA curve second peak maxima for the pastes containing each waste separately. (Second peak refers to calcium silicates hydration exothermic effect)

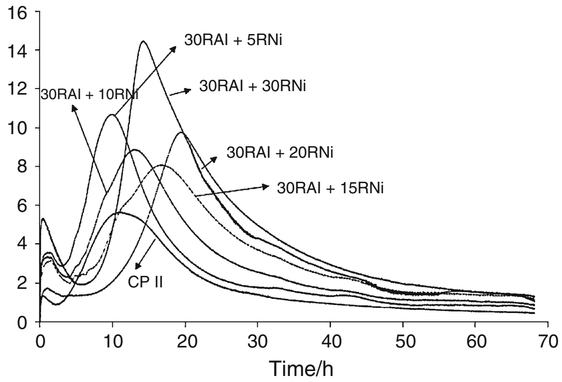

Fig. 7 NCDTA curves of mixed addition pastes with 30 mass% of RAl

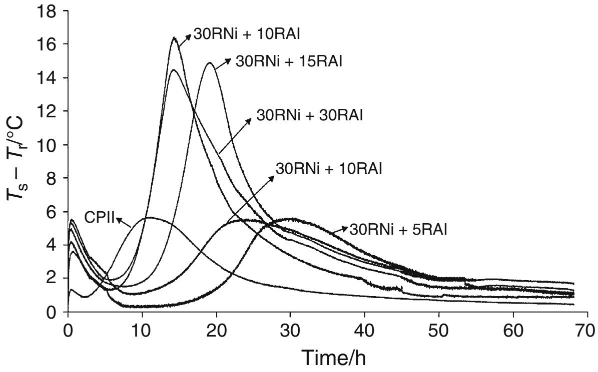

Fig. 8 NCDTA curves of mixed addition pastes with 30 mass% of RNi

Figure 9 shows the time when the maximum of the second NCDTA peak occurs (which refers to tobermorite and calcium hydroxide formation) for the several pastes formed with both wastes addition. There is a clear retarding effect of RNi waste in all cases when it is present on cement hydration. It retards the hydration reactions showing a maximum peak in about 28 h, where was noted the formation of tobermorite, while the cement control paste curve has that peak around 12 h of hydration. From Fig. 9, it can be seen that fixing RNi addition on 30 mass% of cement and increasing the simultaneously added amount of RAl, the overall retarding effect decreases, tending to almost a same time of occurrence of the second peak for the 20 and 30 mass% addition cases of RAl. On the other hand, for the cases where was fixed 30 mass% addition of RAl waste, the presence of increasing additions of RNi delays the occurrence of the calcium silicate hydration step, until 20 mass% addition of RNi, but a different behavior is observed for the case of 30 mass% addition of

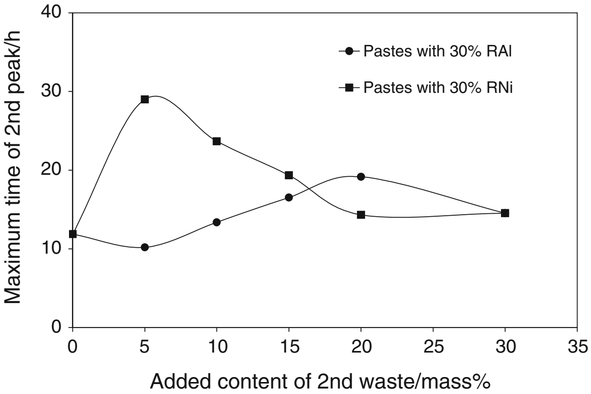

Fig. 9 Influence of simultaneous RAl and RNi additions on the time of maximum tobermorite formation NCDTA peak

this waste. These results show that the hydration process can be controlled within certain limits and that simultaneous use of wastes can be done successfully, because there is an intermediary effect resulting from the simultaneous respective accelerating and retarding actions of each waste (synergic effect) that allows more practical conditions for their solidification process.

To have a complementary information about the main phases formed during hydration in the early stages, TG and DTG analysis data of typical pastes obtained after 4 and 24 h of age are next shown and discussed, as well as the raw materials analyses as received. Figure 10 shows TG and DTG curves of the original cement obtained using a heating rate of 10 °C min^{-1} from room temperature to 1000 °C in air, and of the RNi and RAl wastes done in the same operating conditions, but preceded by an isothermal drying step at 35 °C in the equipment, as was done for all pastes, to better evaluate the mass losses released from their respective dried masses.

From Fig. 10, it can be seen that the calcined masses at 1000 °C of the cement and of RAl and RNi wastes represent, respectively, 95.44, 20.98, and 21.47% of their initial mass. In these two last sample analyses, dried masses at 35 °C were 31.92 and 36.64% of respective initial masses. In the case of RAl, there is an initial mass loss to the hydrated phases present in the waste, followed by a significant DTG peak between 200 and 300 °C, due to the dehydroxylation of the aluminum hydroxide present in the waste. In RNi case, there is an initial mass loss up to 200 °C, mainly due to the nickel hydroxide dehydration, followed by a pyrolysis of the little content of its organic content and from 550 °C the decarbonation of calcium carbonate present in it.

Figure 11 shows the TG curves of typical pastes obtained after 4 h of hydration, on cement initial mass basis in each paste, to have a same basis of comparison. The method used to obtain this curves from their respective TG curves on sample initial mass is detailed on a previous article [37]. Figure 12 shows respective DTG curves on the same basis, in the temperature range where hydrated phases present in each sample release their combined water during analysis.

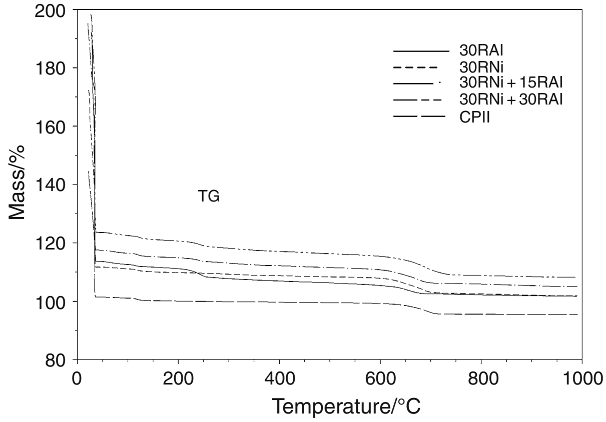

Fig. 11 TG curves of typical pastes after 4 h of hydration on cement initial mass basis

In Fig. 12, up to 100 °C, the first DTG peaks (which actually end by 200 °C) refer to the combined water released from the initially cement hydrated phases (tobermorite + ettringuite) [8] and, in the pastes containing the wastes, from the combined water released from hydrated phases of RAl an RNi wastes. During this mass loss steps, from 100 to 150 °C, the combined water lost from the gypsum phases present in the samples occurs simultaneously [8]. For the samples containing RAl, the third major DTG peaks, which occur mainly from 200 to 300 °C, refer to the dehydration of respective aluminum hydroxide phases, which area increases with increasing content of RAl in the paste. When is the case, from 350 to 450 °C, occurs little DTG peaks due to the dehydroxylation of small calcium hydroxide contents. From 200 to 450 °C also small organic content of residual polyols from the

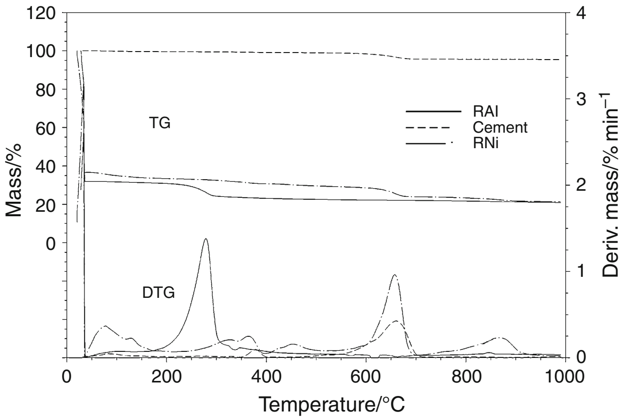

Fig. 10 TG and DTG curves of the original cement and RAl and RNi wastes

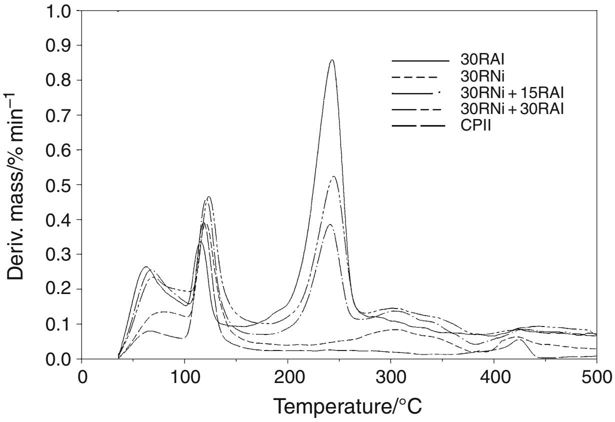

Fig. 12 DTG curves of typical pastes after 4 h of hydration on cement initial mass basis

industrial process are thermally decomposed for the samples that contain RNi.

Figure 13 shows the TG curves of typical pastes obtained after 24 h of hydration, on cement initial mass basis. Figure 14 shows respective DTG curves on the same basis, in the temperature range where combined water is released during analysis.

From Fig. 14, it can be seen that for 24 h of hydration, the paste containing only 30 mass% of RNi still presents a significant gypsum dehydration DTG peak, which indicates, with also the smallest $Ca(OH)_2$ dehydration DTG peak that, even at this time, the cement hydration process was retarded, as was already seen in respective NCDTA curve in Fig. 5. All other samples do not show the presence of gypsum, which indicates that in these cases all gypsum were consumed.

The sample in which it was added only 30 mass% of RAl presented the highest water loss from tobermorite and ettringuite dehydration, as well as the highest combined water loss from $Ca(OH)_2$ dehydroxylation, confirming the acceleration effect of RAl catalytic waste, which was indicated formerly from NCDTA curves in Fig. 4. It can be seen for the pastes containing RAl that, the higher is its content, the higher is the mass loss from aluminum hydroxide and the higher is the water loss from calcium hydroxide dehydroxylation.

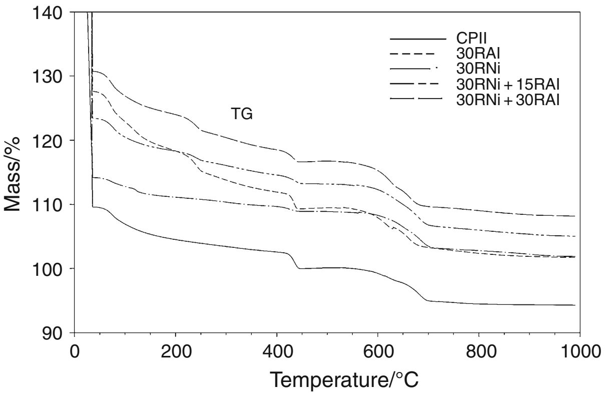

Fig. 13 TG curves of typical pastes after 24 h of hydration on cement initial mass basis

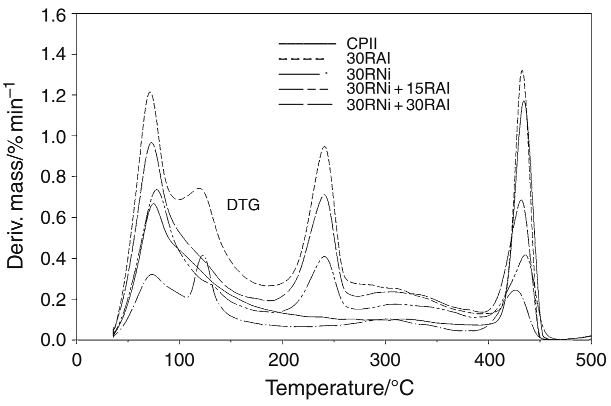

Fig. 14 DTG curves of typical pastes after 24 h of hydration on cement initial mass basis

Figures 11, 12, 13, and 14, as commented previously, refer to the mass losses from cement hydrated phases as well as from the other phases that were already present in each added waste. To see the effect of the presence of each waste on the cement hydration process, a quantitative analysis was done to estimate the total combined water released up to 450 °C, and the combined water released from the main cement hydrated phases during thermogravimetric analysis: (tobermorite + ettringuite) from 35 to 200 °C, gypsum from 100 to 150 °C and for calcium hydroxide from 350 to 450 °C in 4 h cases and from 370 to 470 °C in 24 h cases, which are the respective temperature ranges where calcium hydroxide dehydroxylation occurred. For this purpose, mass losses calculated from TG curves of each waste, proportional to their content in the pastes (transformed to initial cement basis and within respective temperature ranges of each kind of combined water release), were subtracted from the mass losses of TG curves of the samples presented in Figs. 11 and 13 that are also on cement initial mass basis, within same respective temperature ranges. The resulting mass losses of different types of combined water for 4 and 24 h pastes are presented, respectively, in Figs. 15 and 16 as percentages of the initial cement mass of each paste.

From Fig. 15, it can be seen that after 4 h of hydration, the amount of water released from dehydration of gypsum in the pastes containing added wastes is little smaller than in the paste containing only cement and water, indicating as seen in respective NCDTA curves, that the presence of the wastes slightly enhances the initial ettringuite formation during the pre-induction period. Tobermorite and ettringuite released water as well as the water released from calcium hydroxide dehydroxylation present the highest

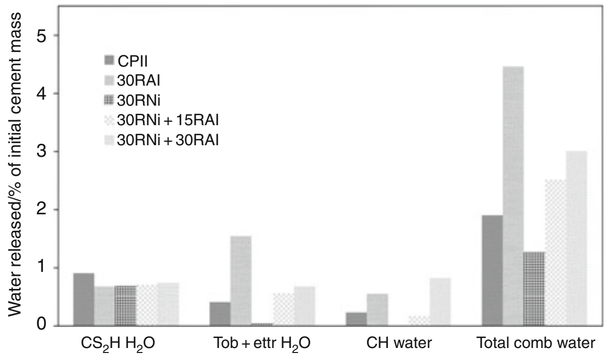

Fig. 15 Combined water released from cement hydrated phases of 4 h pastes (CS 2H H_2O—water from calcium sulfate-dihydrate; tob + ettr H_2O—water from tobermorite and ettringuite; CH water—water from calcium hydroxide)

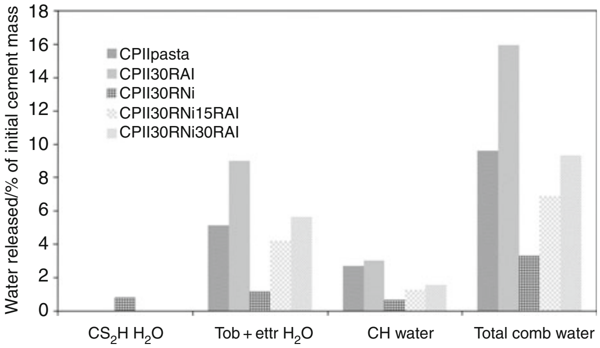

Fig. 16 Combined water released from cement hydrated phases of 24 h pastes (CS 2H H_2O—water from calcium sulfate-dihydrate; tob + ettr H_2O—water from tobermorite and ettringuite; CH water—water from calcium hydroxide)

values for the case containing only 30% of RAl, which confirms the accelerating effect of this waste on the cement hydration accelerating period where tobermorite and calcium hydroxide are formed, as was seen in Fig. 4 NCDTA curves. This effect is also confirmed in the pastes containing 30 mass% of RNi and increasing contents of RAl, where, the higher is the RAl content, the higher is the tobermorite and calcium hydroxide released combined water. Note that, for the case with only 30 mass% of RNi, there is only very small amount of released water from tobermorite and ettringuite and no released water from calcium hydroxide dehydroxylation, which indicates that at 4 h of hydration the accelerating period has not been initiated, confirming what was already seen and concluded from respective NCDTA curve for this paste in Fig. 5.

In a previous study [8], it was seen that for the paste containing only the same kind of cement and water with same water/cement mass ratio, gypsum is totally consumed after 18 h. From Fig. 16, it can be seen that after 24 h of hydration, there is no water released from dehydration of gypsum for all pastes, except for the case with only 30 mass% addition of RNi. This indicates that the complementary gypsum consumption with more ettringuite formation, which occurs during the occurrence of the second highest NCDTA peak and that occurred completely for the other cases, at this hydration time it happened very weakly for the case with only 30 mass% of RNi, because, as seen from Fig. 5, in this case, the duration of the induction period was significantly extended, and the accelerating period has begun after 20 h of hydration, but occurring very weakly up to 26 h of hydration.

From Fig. 16, it can also be seen that tobermorite and ettringuite released water as well as the water released from calcium hydroxide dehydroxylation also present the highest values for the case containing only 30 mass% of RAl after 24 h of hydration, due to the accelerating effect of this waste on cement hydration reactions, as was seen in respective NCDTA curve in Fig. 4, which shows that the second main NCDTA peak was ended by this time. For the pastes containing 30 mass% of RNi and increasing contents of RAl, the lower is the RAl content, the lower is the tobermorite and calcium hydroxide released combined water and in lower quantities than in only 30 mass% of RAl case, what could be previewed from the time when their respective second NCDTA peaks have ended in Fig. 8 at hydration times higher than 24 h. Note that for the case with only 30 mass% of RNi, there is only a very small amount of released water from tobermorite and ettringuite and from calcium hydroxide dehydroxylation when compared to the other cases, due to the fact that, as seen from its NCDTA curve in Fig. 5, the accelerating period begins only after 20 h of hydration and occurs very weakly within the 20–24 h period of hydration.

Conclusions

- Non-conventional differential thermal analysis (NCDTA) is a very practical tool to analyze retarding or accelerating effects on cement hydration due to the presence of wastes during their S/E process with cement.
- In the early stages of solidification with cement, hydration retarding and accelerating effects occur, respectively due to RNi and RAl presence, with significant thermal effects.
- When only the RNI catalyst waste is used, the higher is its added content, the higher is its retarding effect on the solidification during tobermorite and calcium hydroxide formation, and this effect is a linear function of the added content
- When only the RAl catalyst waste is used, the higher is its added content, the higher is its accelerating effect on the solidification process due to the increase of the initial ettringuite formation, but this effect decreases non linearly as the added RAl content increases.
- During the simultaneous use of the two waste catalysts in their stabilization process by solidification in cement there is a synergic effect, which allows more practical hydration conditions than when using each catalyst waste separately.
- From the TG and DTG curves on cement initial mass basis of the several pastes obtained at 4 and 24 h of hydration and from TG and DTG curves of each waste obtained on same operating conditions and same basis, the combined water released from the main cement hydrated phases existent in each paste can be estimated.
- These data, which allow a better understanding of what happens during the early stages of cement hydration with the formation or consumption of the main cement hydrated phases due to the catalyst wastes presence, confirm the same accelerating or retarding effects that

were indicated directly from respective NCDTA curve analysis for each case.

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References

1. Chen QY, Tyrer M, Hills CD, Yang XM, Carey P. Immobilization of heavy metal in cement-based solidification/stabilization—a review. Waste Manag. 2009;29:390–403.
2. Cioffi R, Lavorgna M, Santoro L. Environmental and technological effectiveness of a process for the stabilization of a galvanic sludge. J Hazard Mater. 2002;89:165–75.
3. Kindness A, Lachowski EE, Minocha AK, Glasser FP. Immobilisation and fixation of molybdenum (VI) by Portland cement. Waste Manag. 1994;14:97–102.
4. Minocha AK, Jain N, Verma CL. Effect inorganic materials on solidification of heavy metal sludge. Cem Concr Res. 2003;33:1695–701.
5. Dweck J, Buchler PM, Coelho ACV. Solidification/stabilization of a tannery waste with blended cement and wyoming bentonite. J Environ Sci Health. 2000;35:715–40.
6. Lin CK, Chen JN, An Lin CC, MR N. XRD and EDS study of solidification/stabilization of chromium with Portland cement and C3S. J Hazard Mater. 1997;56:21–34.
7. Shi C, Spence R. Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes. Crit Rev Environ Sci Technol. 2004;34:391–417.
8. Dweck J, Buchler PM, Coelho ACV, Cartledge FK. Hydration of a Portland cement blended with calcium carbonate. Thermochim Acta. 2000;346:105–13.
9. Winnefeld F, Barlag S. Calorimetric and thermogravimetric study on the influence of calcium sulfate on the hydration of ye'elimite. J Therm Anal Calorim. 2010;101:949–57.
10. Vespa MR, Dahn R, Grolimund D, Harfouche M, Wieland E, Scheidegger AM. Speciation of heavy metals in cement-stabilized waste forms: a micro-spectroscopic study. J Geochem Explor. 2006;88:77–80.
11. Lange LC, Hills CD, Poole AB. The effect of accelerated carbonation on the properties of cement solidified waste forms. Waste Manag. 1996;16:757–63.
12. Salhan A, Billinghan J, King AC. The effect of a retarder on the early stages of the hydration of tricalcium silicate. J Eng Math. 2003;3–4:367–77.
13. Poon CS, Peters DJ, Perry R, Barnes P, Barker AP. Mechanisms of metal stabilization in cement based fixation processes. Sci Total Environ. 1985;41:55–71.
14. Poon CS, Clark AI, Perry R. Permeability study of the cement based solidification process for the disposal of hazardous wastes. Cem Concr Res. 1986;16:161–72.
15. Brandštetr J, Polcer J, Krátký J, Rolešinský R, Havlica J. Possibilities of the use of isoperibolic calorimetry for assessing the hydration behavior of cementitious systems. Cem Concr Res. 2001;31:941–7.
16. Wczelik WN. Calorimetry in the studies of cement–Pb compounds interaction. J Therm Anal Calorim. 2007;88:291–4.
17. Ježo L, Palou M, Kozánková J, Ifka T. Determination of activation effect of $Ca(OH)_2$ upon the hydration of BFS and related heat by isothermal calorimeter. J Therm Anal Calorim. 2010;101:585–93.
18. Cunha ALC, Gonçalvez JP, Cartledge FK, Filho RDT, Dweck J. Evaluation of the metakaolin pozzolanic reactivity in cement pastes. Mater Sci Forum. 2008;591–593:827–32.
19. Gawlicki M, Wczelic WN, Bak L. Calorimetry in the studies of cement hydration: setting and hardening of Portland cement–calcium aluminate cement mixtures. J Therm Anal Calorim. 2010;100:571–6.
20. Pacewska B, Wilińska I, Blonkowski G. Investigation of cement early hydration in the presence of chemically activated fly ash: use of calorimetry and infrared absorption methods. J Therm Anal Calorim. 2008;93:769–76.
21. Lou W, Guan B, Wu Z. Calorimetric study of ternary binder of calcium aluminate cement, Portland-limestone cement and FGD gypsum. J Therm Anal Calorim. 2010;101:119–27.
22. Kadri EH, Duval R. Hydration heat kinetics of concrete with silica fume. Constr Build Mater. 2009;23:3388–92.
23. Cheren da Cunha AL, Gonçalves JP, Büchler PM, Dweck J. Effect of metakaolin pozzolanic activity in the early stages of cement type II paste and mortar hydration. J Therm Anal Calorim. 2008;92:115–9.
24. Pinto CA, Dweck J, Sansalone JJ, Cartledge FK, Tittlebaum ME, Büchler PM. Early stages of solidification/stabilization of storm water runoff solid residuals in cement. J Therm Anal Calorim. 2005;80:715–20.
25. Technical Standards of Brazilian Association (ABNT), NBR 10.004. Solid waste—classification. 2004 (in Portuguese).
26. Dweck J, Buchler PM, Aderne RS, Silva PFF, Coelho ACV, Cartledge FK. Evaluation cement hydration by non-conventional DTA: an application to waste solidification. J Therm Anal Calorim. 2003;71:821–7.
27. Glasser FB. Fundamental aspects of cement solidification and stabilization. J Hazard Mater. 1997;52:151–70.
28. Alberoni VG. Solidification/stabilization process of an industrial waste containing nickel. M.Sc. Dissertation, School of Chemistry, Rio de Janeiro University. 2005:1–98 (in Portuguese).
29. Silva DM. Solidification/stabilization process of an industrial waste containing aluminum. M.Sc. Dissertation, School of Chemistry, Rio de Janeiro University. 2005:1–99 (in Portuguese).
30. Technical Standards of Brazilian Association (ABNT), NBR 10.005. Leaching of solid residues—procedure. 2004 (in Portuguese).
31. Environmental Protection Authority (EPA). Environmental guidelines: assessment, classification and management of liquid and non-liquid wastes (ISBN 0 7313 0215 X, EPA 99/21). Australia: Sydney; 1999.
32. Pinto CA, Buchler PM, Dweck J. Pozzolanic properties of a residual FCC catalyst during the early stages of cement hydration. J Therm Anal Calorim. 2007;87:715–20.
33. Krielow E. A screening assessment of solidification/stabilization for storm water residuals. M.Sc. Thesis, Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College, 2003:1–202.
34. Scheidegger AM, Wieland E, Dahn R, Spieler P. Spectroscopic evidence for the formation of layered Ni–Al double hydroxides in cement. Environ Sci Technol. 2000;34:4545–8.
35. Scheidegger AM, Wieland E, Scheinost AC, Dahn R, Tits J, Spieler P. Ni phases formed in cement and cement systems under highly alkaline conditions: an XAFS study. J Synchrotron Radiat. 2001;8:916–8.
36. Pinto CA, Hamassaki LT, Diaz FRV, Dweck J, Buchler PM. Tannery waste solidification and stabilization. J Therm Anal Calorim. 2004;77:777–87.
37. Dweck J, Cherem da Cunha AL, Pinto CA, Gonçalves JP, Büchler PM. Thermogravimetry on calcined mass basis: hydrated cement phases and pozzolanic activity quantitative analysis. J Therm Anal Calorim. 2009;97:85–9.