Journal of Architectural Design and Construction Technology
Volume 2 | Issue 1

Research Article Open Access

Characterization of Dolostone Filler in Blended Cements

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Citation: ADS Barsi, MA Trezza, EF Irassar. Characterization of Dolostone Filler in Blended Cements. J Arch Des Cons Tech (2021);2(1):37-43.

Received Date: December 03, 2020; **Accepted Date:** February 26, 2021; **Published Date:** March 08, 2021

Abstract

This paper reports the results of the characterization of dolostone from a quarry of Sierras Bayas, Province of Buenos Aires, Argentina, by means of XRD and FTIR, for its application as Supplementary Cementitious Material (SCM) in blended cements. The objective is to study the behaviour of cement pastes and mortars with dolostone filler addition and to consider its use as alternative to limestone. Blended cements with 0, 10, 20 and 30 % dolostone filler replacements were prepared and the heat release rate, the flowability and the setting time of the cement pastes with a w/cm ratio of 0.4 were measured. It was found that, the flowability and the setting time, decreased as the filler content increased. Compressive strength of blended mortars (w/cm=0.50) were lower than that OPC mortar at all percentages and ages studied (1 to 90 days).

Key Words: Dolostone; Filler; Blended Cements; Sustainability; Calorimetry

1. Introduction

The addition of supplementary cementitious materials (SCM) to clinker portland has increased due to technological, economic and ecological reasons [1]. Currently, the sustainability of industry requires incorporating raw materials with low energy embodied. In this context, hydraulically active (pozzolans and blast furnace slags) or hydraulically inactive (fillers) SCM appear as great candidate to use during blended cement manufacturing, because they only consume energy for grinding [2]. SCM are incorporated into the grinder with clinker and gypsum to produce blended cements, or ground separately and mixed to produce "tailor-made cements" or concrete as occurred in self-compacting concretes [2]. The grindability and availability of SCM are the main factors for their use. Among the SCM, carbonates are easier to grind than the slag and siliceous pozzolans (volcanic glass and tuff). Several investigations [3-5] have shown that the addition of natural pozzolans and granulated blast furnace slag improves the properties of concrete. However, the worldwide supply of these SCM is limited to some regions and the slag is scarce when it is compared to the annual demand for concrete.

Carbonate rocks are generally available near to cement factory. Different authors used these rocks as aggregates and / or cement replacement, up to 30 % in concrete, whit great improvements in their mechanical and durability properties [6-7]. In other hand, fillers are added in order to increase the cement production without increases the CO_2-emission to obtain a blended cement with a given strength class. The dilution of the cement and the modification of the particle size distribution appear as consequence of Portland cement replacement by limestone filler. Another effect is the heterogeneous nucleation that stimulate the Portland cement hydration [8]. There is no single and universal definition of fillers, but they can be defined as fine particle materials that are inert or almost chemically inert when mixed with cement [9]. The beneficial effect of the filler depends on the fineness of the material, since the decrease in particle size contributed to the nucleation; the replacement percentage, because as it increases the dilution effect is predominant [10]; and the affinity of the filler with cement hydrates that is related to the nature of the mineral used [11].

The first recorded of filler use was at Elephant Butte and

Arrowrock dams, built by the US Bureau of Reclamation between 1912 and 1916, where ~ 47 % of Portland cement was replaced by granite dust [9]. Many investigations [12-13] have determined that the filler addition improves the performance of cements, mortars and concretes. Lawrence et al. [14] confirmed the improvement of cement hydration with quartz fillers.

Generally, standards limit the composition of the calcareous material to be used as filler. The Argentine (IRAM 1593: 94) and the European standard (EN 197: 11) limit the content of CaO expressed as calcium carbonate $CaCO_3$ in ≥ 75 %; while the ASTM C-150: 12 standard limits to ≥ 70 %. The use of fillers other than limestone is allowed only as minor mineral component (< 5 %) in blended cements according to EN 197 and IRAM 50000. Then, in the cement field when talking about filler in cements, reference is made to those of limestone nature exclusively. However, many raw deposits do not meet the composition requirement, and they can have the same effects when are appropriately ground.

Several investigations explored the dolomitic filler as alternative. Xu et al. [15] studied the behaviour of mortars with filler at 40 °C and found that the compressive strength of mortars with replacements ≥ 20 % of dolomitic filler at 90 days was greater than that corresponding to mortars with limestone filler. Schöne et al. [16] found similar values of compressive strength in mortars with 23 % dolostone or limestone filler. The main shortcoming of dolomite is its mineral instability in highly alkaline environments such as the cement paste, since the dedolomitization phenomenon occurs [17]. However, recent studies [18-20] showed that the presence of other ions (Al, Si) change the dolomite reaction producing hydration products similar to those of limestone Portland cement. These results induced a renewed interest to use other type of calcareous filler as SCM.

The purpose of this study is to investigate the effect of dolostone filler on the physical properties of blended cement containing 0 to 30 % of replacement by mass. The early effects on the heat of hydration, flowability and setting time were determined for this filler and the later effect on compressive strength of standard mortar.

2. Materials and Methods

An Ordinary Portland Cement (OPC) provided by Loma Negra CIASA (Olavarría, Province of Buenos Aires, Argentina) and dolostone (D) from the PolceCal SA quarry (Sierras Bayas, Province of Buenos Aires, Argentina) were used. Table 1 reports the chemical composition of the OPC and D-filler determined by XRF. The mineralogical composition of the OPC was C_3S: 60.0 %; C_2S: 13.3 %; C_3A: 3.3 %; C_4AF: 12.2 %; gypsum 5.0 % and 4.8 % limestone as minority component according the cement manufacturer data. The CaO content in D-filler expressed as $CaCO_3$ was 54.6 %, lower than the limit established by standard (75 %) to be used as calcareous filler in blended cement.

Table 1: Chemical composition of OPC and D-filler

	OPC [%]	D-filler [%]
SiO_2	20.21	3.59
Al_2O_3	3.81	0.63
Fe_2O_3	4.01	0.82
CaO	60.30	30.60
MgO	0.53	19.40
SO_3	3.08	0.02
K_2O	1.06	0.21
Na_2O	0.05	0.06
LOI	2.50	44.78

Figure 1 shows the XRD-pattern for the dolostone. The main mineral was dolomite and its minor phases were calcite, quartz and illite. The mineralogical composition obtained by Rietveld method with HighScore© software was 90.5 % of dolomite, 3.0 % of calcite, 3.0 % of illite and 3.5 % quartz. FTIR spectroscopy (Figure 1) allowed to characterize dolomite by the carbonate group (νi-CO_3^{2-}) with characteristic bands at 1440 (ν3), 880 (ν2) and 728 (ν4) cm^{-1}, and it was a calcite-like structure. Bands at 1090, 780-800 and 518 cm^{-1} were assigned to quartz (Q).

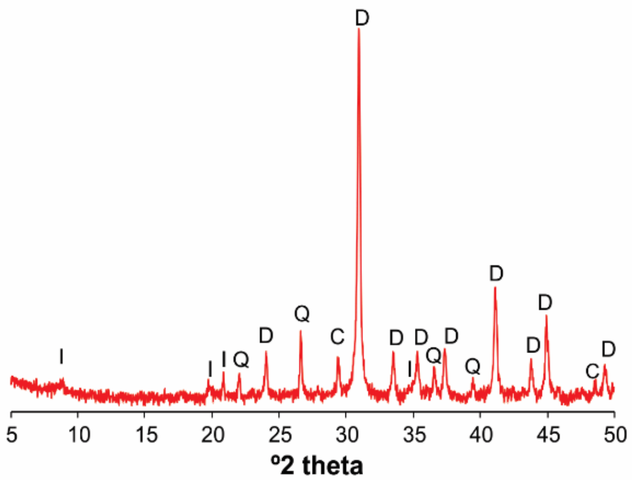

Figure 1: XRD pattern of dolostone

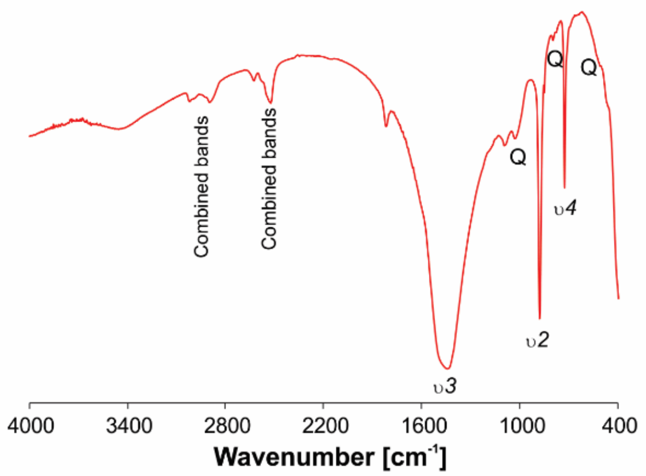

Figure 2: FTIR spectra of dolostone
D: dolomite; C: calcite; I: illite; Q: quartz

D-filler was obtained by grinding 2 kg of dolostone in a laboratory ball mill with programmed time. During the first batch, its particle size distribution (PSD) was evaluated every 30 min using the particle size analyser by laser diffraction (Malvern Mastersizer 2000-E) with Sirocco 2000-M dry dispersion unit to determine the grinding time. After 120 min, the grinding objective (d_{50}< 4 µm) was attained and the grinding time established. Thereafter, 10 kg of D-filler was obtained in five grinding batches. For the homogenized sample, the d_{10}, d_{50} and d_{90} parameters of PSD, the relative density (ASTM C 127) [21] and the specific surface area using the Blaine test method (ASTM C 204) [22] were determined. Table 2 reports the physical properties of used materials. Figure 3 shows the fractional volume and cumulative volume of PSD curves for OPC and D-filler. D-filler has a bimodal PSD curve with modes at ~ 3 and 20 µm; while the OPC curve had a unique mode at 30 µm.

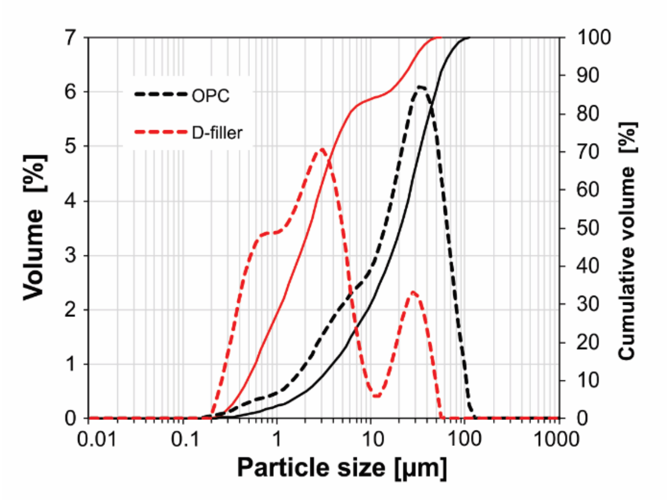

Figure 3: PSD and cumulative volume curve of OPC and D-filler

Table 2: Physical characteristics of OPC and D-filler

	OPC	D-filler
Particle size distribution		
d_{10} [µm]	2.97	0.52
d_{50} [µm]	21.77	2.34
d_{90} [µm]	58.42	23.79
Density [g/cm^3]	3.13	2.86
Specific surface area [m^2/kg]	336	614

Blended cements were prepared replacing 0, 10, 20 and 30 % of D-filler by mass of OPC; and they were called C0, C10D, C20D and C30D, respectively. The studies performed on cement pastes with water-to-cementitious material ratio (w/cm) of 0.40 were: the rate and the cumulative heat release, the flowability and the setting time. The hydration heat released was measured using a conduction calorimetry during 48 hours under isothermal conditions at 20 ºC. The initial mini-slump test was determined as the average of spread diameter of paste and the mini-slump loss was measured up to 120 min every 30 min using the Kantro cone [19]. The setting time was measured using the Vicat test apparatus (EN 196-3) [23].

Mortars (cement/standard sand 1:3 and w/cm = 0.5) were elaborated according the EN 196-1 procedure [24] and they were called: M-C0, M-C10D, M-C20D and M-C30D. After mixing, the mortar flow (ASTM C 1437 [25]) was determined and the prism specimens (40 × 40 × 160 mm) were cast and cured during 24 h in the moist cabinet, removed from the moulds and then immersed in water at 20 ºC up to the test age. Compressive strength was determined on four specimens at 1, 2, 7, 28 and 90 days. The efficiency of filler was measured by the compressive strength index (CSI) calculated as equation (1):

$$CSI[\%] = \left(\frac{R_{M-CX}}{R_{M-C0}}\right)*100........(1)$$

where R_{M-CX} is the compressive strength of the mortar with D-filler and the R_{M-C0} is the compressive strength of the OPC mortar at the same test age.

3. Result and Discussion

Calorimetric curve

Figure 4 shows the rate of heat evolution (mW/g) and the cumulative heat release (J/g) for blended cements with a typical calorimetric curve. Firstly, a high rate of heat released is attributed to the dissolution process and very early hydration of aluminate phases. Then, the dormant period has low rate during the concentration of species in solution increases until promoting the C_3S reaction. The acceleration of hydration reactions due to the C_3S hydration with the initial precipitation of the C-S-H and CH [26]. The third peak is attributable to the sulphate depletion due to the renewed ettringite (AFt) formation was observed as a shoulder. This peak had low intensity due to the low C_3A content of the cement (3.3 %). Finally, hydration reactions slow down gradually without significant point in the descending branch reaching to a very low heat rate after 2 days [27].

When the D-filler was added, the heat rate was changed in accordance with the reported by Ye [28]. The duration of the dormant period was in the same range (160 min) for the OPC and the different replacements of D-filler. During the acceleration period, the slope of the curve increases with the presence of D-filler (0.0026, 0.0036, 0.0033 y 0.0034 mW/g.min of C0, C10D, C20D y C30D respectively) indicating the stimulation caused by fine filler particles on the hydration of OPC. The second peak intensity is the same instead the reduction of clinker fraction caused by the D-filler replacement and the maximum values were 1.08, 1.14, 1.12 and 1.10 mW/g of C0, C10D, C20D and C30D, respectively. The third peak was more pronounced for blended cements with D-filler. Bentz [29] reported the same behaviour on OPC: limestone filler systems varying from 100 to 5 % of OPC and it was attributed to the contribution of finer particles to the heterogeneous precipitation that increases the sulphate depletion causing a more pronounced reaction of aluminate phases.

Figure 4 also shows that the cumulated heat Qt (J/g) of the pastes with 10, 20 and 30 % D-filler are similar to each other and to that corresponding to C0. The cumulative heat is fairly independent

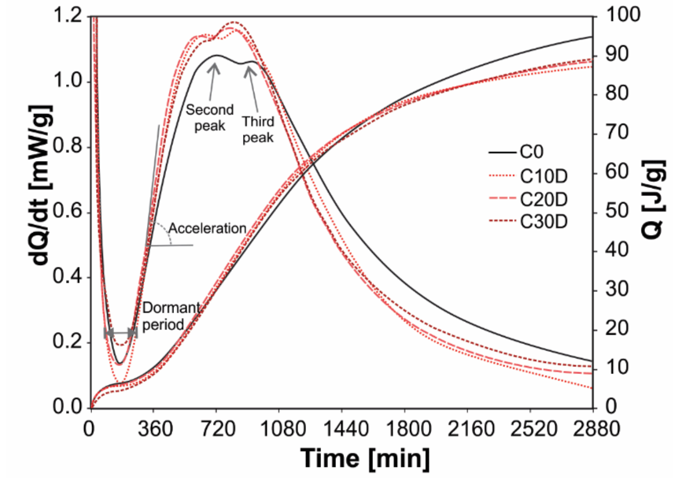

Figure 4: Heat release rate and cumulative heat for D-filler pastes

of filler level during the first 12 h as reported by Bentz [29]. However, the heat released at 48 h was different: C0 has ~94 J/g, while the C10D, C20D and C30D as slightly low value (~ 87 J/g).

Flowability

Figure 5 shows the spread diameter as function of D-filler replacement. For initial mini-slump (0 min), the spread diameter of paste decreases progressively with increases D-filler content. The initial spread diameter (80 mm) of C0 was reduced in 12.5 % for 30 % the D-filler. This reduction is attributable to the large specific surface area of dolostone (see Table 2), that increases the water demand needed to wet the grains instead the better packing of blended cement with filler [30]. This shortcoming of D-filler could be improved using a superplasticizer to disperse the very fine particles. On the other hand, the mini-slump loss was less significant for paste with increasing percentage of D-filler. The spread diameter reduction of C0 paste was from 80 mm to 63 mm and 56 mm at 60 and 120 min, respectively; representing a mini slump loss higher than 20 % during the first hour.

For C30D paste, the mini-slump loss was form 60 % and 54 during 60 and 120 min. The influence of D-filler content on the mini-slump loss was reduced with the elapsed time. It was more markedly at 30 min (6.9 %), and then it was less significant (5.6

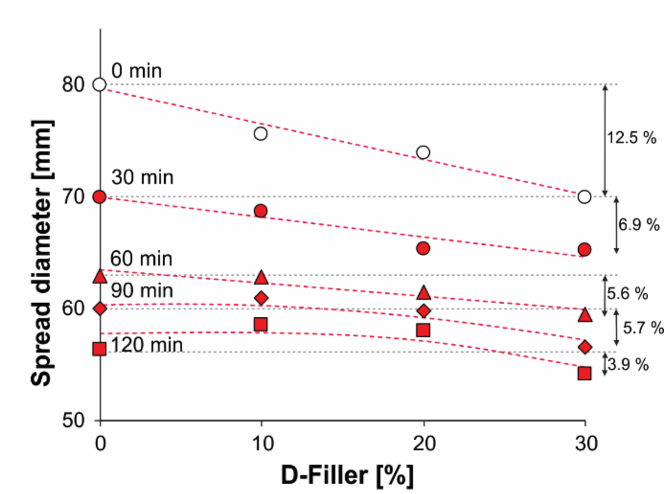

Figure 5: Diameter-filler percentage curve of pastes

to 3.9 %) near to the experimental error. It is attributed to the less water requirement to form early hydrated compounds when increases the replacement level.

Setting time

The initial and final setting times are shown in Figure 6. The pastes with D-filler have shorter setting times than the corresponding to C0 paste and the setting time occurs earlier as the percentage of D-filler increases.The setting time is closely related to the early hydration kinetics and the distance between the particles. It marks the formation of the first percolated structure through the interconnection of solid particles and hydration products [31]. The incorporation of filler reduces the initial setting time because it increases the hydration degree of cement due to heterogeneous nucleation [32-33] and the reduction in the interparticle distance. Moon et al. [34] showed that setting times decreased with increasing limestone content (from 15 to 35%). D-filler has a similar behaviour to the limestone filler and this is attributed to the high hydration

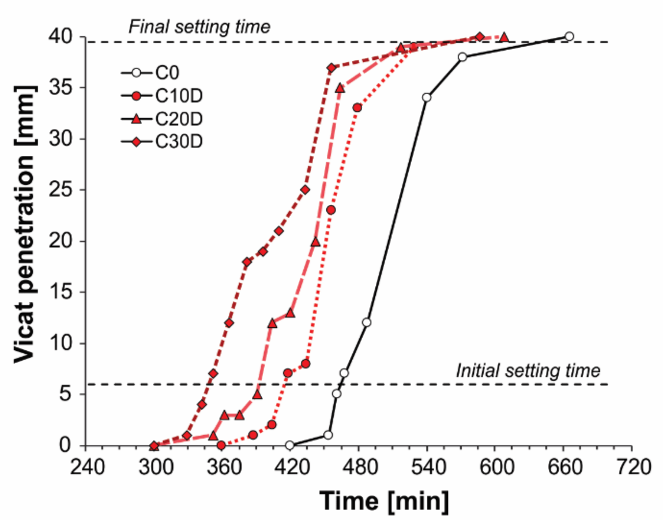

Figure 6: Setting times of pastes

of C_3S and C_3A during the initial stages, in line with the observed in calorimetric tests. Also, the lower interparticle distance in the blended cement can contribute to earlier setting [30].

Mortar flow, compression strength and CSI

As occurred on paste flowability, the mortar flow (Table 3) slightly decreased when increased the D-filler content. These results agree with the experiences reported by de la Cuesta Martinez et al. [35] for mortars containing dolomitic fillers (0 to 30 % by weight replacement) with different fineness (124 to 399 m2/kg specific surface area Blaine). Figure 7 shows the compressive strength as function of the filler content. For all ages, the compressive strength of blended cements was lower than the corresponding to the M-C0, and it decreased when D- filler content increased. These results were in line with those reported by Xu et al. [15]. They found that the compressive strength of mortar (w/c = 0.50) of blended cements containing 10, 20 and 30 % of dolomitic filler were lower than the corresponding to the OPC mortar up to 90 days. It is

Table 3: Flow of mortar

Mortar	Flow [%]
M-C0	124 ± 0.8
M-C10D	124 ± 0.6
M-C20D	122 ± 0.3
M-C30D	117 ± 0.3

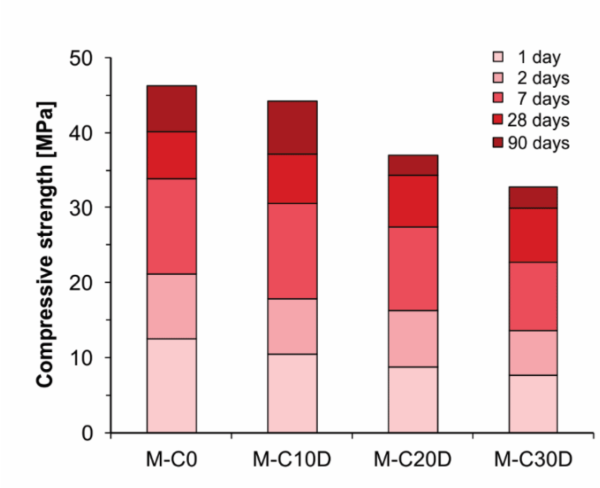

Figure 7: Compressive strength

attributed to the dilution effect that reduces the volume of cement available to react at early age increasing the effective w/c that could not be compensated by the stimulation of cement hydration OPC.

Figure 8 shows the CSI values of blended cements. For all D-filler percentages and all ages studied, the CSI were lower than 100. In this figure, the dotted line indicates the 90, 80 and 70 that represent the addition replacement. For C10D and C20D blended

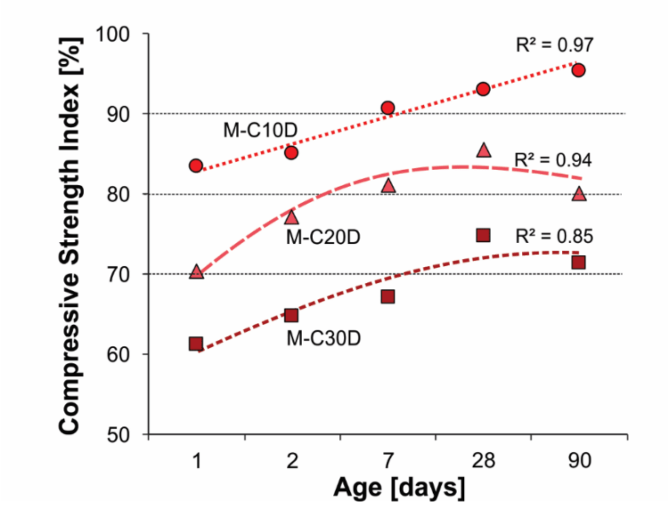

Figure 8: Compressive strength index of mortars

cements, the dilution effect is partial compensated after 7 days and it occurs at 28 days for C30D. Mortars with D-filler do not exceed the dilution effect at early ages. However, this trend was inverted at 28 days and it could be attributed to some reaction of dolostone to form hydrotalcite-like compound [19].

4. Conclusions

Based on the results of the present study, it can have concluded that effect of dolostone filler on the physical properties of blended cement are:

- The addition of D-filler stimulates the hydration of OPC, as indicate the parameters of the calorimetric curves: the acceleration slope and the intensity of second peak are higher than the OPC despite the dilution effect. Stimulation effect occurs for all percentage used (10, 20 and 30 %).

- The initial mini-slump decreases when the D-filler content increases. The mini-slump loss of D-filler pastes was lower than that OPC attaining to similar mini-slump-value after 120 min.

- The setting time decreases when increases the partial replacement of cement by D-filler.

- As the replacement of cement by D-filler increases, the compressive strength decreases for all ages studied and it is attributed to the dilution effect.

- At early ages, the stimulation effect does not compensate the dilution effect for blended cement with D-filler. However, after 28 days the trend is reversed indicating other effect that contribute to the strength and should be investigated.

These results indicate that the use of dolostone as SCM can be considered interesting alternative, but deeper studies will be made to reveal its stability and later strength contribution.

5. Acknowledgements

This work was supported by the CICPBA and CONICET (PIO) and the Universidad Nacional del Centro de la Provincia de Buenos Aires (Project E02/122). Di Salvo Barsi acknowledges to the join fellowship CICPBA-UNCPBA program.

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