



BIOPOLYMERS: A NEW WAY FOR THE PROTECTION OF CONCRETE STEEL REINFORCEMENTS

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1. INTRODUCTION

The aim of this study is to develop products made with biological components allowing to develop more eco-friendly concrete. It contributes to the effort in sustainable development that consists to limit the impact of buildings on environment and humans, with a guarantee of better quality concerning esthetical, durability and resistance criteria. In order to reduce CO₂ release associated with the clinker production, it appears of primary importance to develop the use of concrete containing products like Ground Granulated Blast-furnace Slag (GGBS). Concrete with GGBS containing biopolymers should be more durable and the biopolymers could allow the curing and preservation of more aged works. The goals concerning sustainable building are:

- To use recyclable material during the building in order to preserve natural resources,
- To control the aging of works

Among the many pathologies affecting the reinforced concrete works, the rebars corrosion in one of the most

frequently found and can induce the failure of the structure [1]. Although initially protected by the alkalinity of the sound concrete, (pH about 13), the rebars environment may change because of the pH decrease due to the cement matrix carbonation [2-4] and/or to the penetration of aggressive chemicals compounds such as chloride ions through the porous network [5, 6]. The rebars corrosion leads to an increase of their volume up to 9 times the volume of the not corroded rebars [7] and can then induce the cracking of the embedding concrete. The classical solutions against rebars corrosion are: (i) increase of the embedding depth as specified by standards [8], (ii) cathodic protection of the rebars [9, 10] and (iii) impregnation of water repellent or corrosion inhibitor on concrete surface [11]. At the present time, about 20 patents describe corrosion inhibition products as additives in fresh concrete or to apply on hardened concrete. Those inhibitors are made of chemical substances listed in table 1 (table 1), few of them are not eco-friendly regarding the pictogram of their Sanitary and Environmental Data Cards (FDES).





Chemical Substances	Eco-friendly	Not eco-friendly
Alkaline metals		x
Hydroxylamines		x
Silane/Siloxane		x
Sodium gluconates	x	
Aluminium nitrates		x
Sodium Molybdates		x
Ammonium benzoates		x
Alkaline-earth nitrite metals		x
Alkaline-earth nitrate metals		x

Table 1: Chemical substances present in corrosion inhibitors for concrete rebars

Some bacterial species secrete biopolymers, called Extracellular Polymeric Substances (EPS), aiming to protect cells when their environment becomes aggressive and to increase their adhesion on surfaces by forming biofilms [12]. Among these biopolymers, the EPS 180 are exopolysaccharides secreted by the *Lactobacillus reuteri* bacteria. They have already showed corrosion inhibiting properties on steel in seawater [13, 14].

This study aims to develop a new eco-friendly way to protect rebars against corrosion by using biopolymers as admixtures in cement based materials. Furthermore, the associations of this admixture with cement containing GGBS will contribute to develop sustainable building. In a first step, we have evaluated the influence of EPS 180 in admixture incorporated in cement pastes on the corrosion of low-carbon steel rebars. Open circuit potential (OCP) measurements and electrochemical impedance spectroscopy tests were carried out on C15 steel rebars in CEM I and CEM V/A cement pastes immersed in natural seawater.

In order to protect monuments, corrosion inhibitors are applied on the surface of concrete, it is why the EPS 180 were also incorporated in a solution applied on the cement surface. In this case, the protection against corrosion is more often due to the reduction of penetration towards the concrete of aggressive elements present in the water than to a direct inhibiting action on the rebars surfaces. The corrosion inhibitors are effectively able to clog the concrete porous network and then to decrease the capillary imbibition rate of concrete [15]. For this study, the capillary behaviours of samples sprayed or painted with a solution containing EPS 180 and of samples containing an admixture with EPS 180 were compared. Capillary imbibition tests were carried out on cement paste and mortars to characterize the influence of the biopolymer (EPS 180) on the porous network and the hydric transfers of cement pastes and mortar.

2. MATERIAL AND METHODS

EPS 180 are natural extracellular polymeric substances secreted by the gram-positives bacteria *Lactobacillus reuteri* from sucrose thanks to the glucansucrase GTF 180 enzyme [16]. These biopolymers are safe for Human people: the patent [17] describing it specifies that the *Lactobacillus reuteri* bacteria can be used in food industry. EPS 180 are furnished as dehydrated powder and are dissolved in distilled water at 1.3 g/l concentration. The proportion of the admixture water free for the cement grain hydration is estimated at 50% of the total EPS 180 admixture volume. This EPS 180 solution is considered as an admixture regarding the NF EN 934-2 French standard: the admixture content in the sample is limited to 5% of the cement mass.

The samples were manufactured using two cement bases: one ordinary Portland cement CEM I 42.5 R CE CPS (95,5% clinker, 4,5% GGBS, Blaine fineness: 3750 cm²/g) and one composed cement CEM V/A (S-V) 32,5N PM-ES CP1 (51 % clinker, 23% GGBS and 26% siliceous fly ashes, Blaine fineness: 4400 cm²/g).

The cement paste batch was composed of 180 grams water and 450 grams cement, i.e. the mass ratio water/cement is 0.4. The mortars samples were manufactured according to the procedure described by the European standard [18]. The mortar batch was composed of 225 grams water, 450 grams cement and 1350 grams standard sand, i.e. the mass ratio water/cement was 0.5. The EPS 180 admixture contents in the samples batches were 0%, 0,5%, 1% and 2,5% of the cement mass of the cement paste samples; 0%, 2,5% and 5% for the mortars. The electrochemical tests were carried out on cement pastes reinforced with C15 low-carbon steel rebars. Capillary imbibition tests were carried out on cement paste and mortar samples.

The electrodes modeling the reinforcing bars were C15 steel bars 8 mm in diameter, 22 mm length and their extremities are polished. A copper wire was hammered and tin brazed at upper side of the rebars and each end was covered with insulating varnish as shown by Figure 1. Samples were molded as 2 cm edge cubes and the rebars were placed in their vertical axis. After 28 days standard curing (20°C±2°C, RH>90%) these samples were immersed in the natural running seawater in Den Helder harbor (Netherlands).

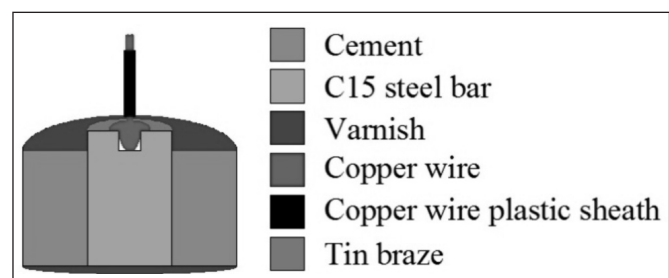


Figure 1: Cement reinforced with C15 steel for corrosion tests

Open circuit potential was measured according to the time with a Keithley 191 multimeter and a silver – silver chloride / potassium chloride reference electrode ($E_{Ag-AgCl/ESH} = 0.197V$, $E_{Ag-AgCl/SCE} = -0.045V$).





Electrochemical impedance spectroscopy (EIS) tests were carried out using:

- a measurement cell: platinum counter electrode, Ag/AgCl-KCl electrode and working electrode (sample)
 - a Faraday cage for protection against external electromagnetic perturbation
 - a potentiostat: Solartron SI 1286 electrochemical interface and Solartron SI 1255 frequency response analyzer.
- The electrolyte was natural seawater and tests did not start before OCP stabilization. This potential was then imposed by the potentiostat. The results obtained were analyzed using Zview[®] software. The EIS parameters used were signal amplitude of ± 10 mV vs. OCP, a frequency range from 100 kHz down to 1 mHz and a measurements step of 5 points per decade.

For the capillary imbibition tests, samples were firstly molded as 5 cm edge cubes and the sawed in four 50x25x25 mm³ parallelepiped samples. Four cement paste samples were studied: the reference samples without EPS 180, samples with EPS 108 solution used as admixture (5% of the cement mass), samples covered with EPS 180 solution by painting or spraying. Two types of mortars were used: the reference samples without EPS 180, samples with EPS 180 solution used as admixture (5% of the cement mass).

Before capillary imbibition tests, samples were vacuum

dried (pressure lower than 50 μ m mercury – 6.7 Pa) and then stocked in a dessicator until the test. The tests were carried out in an opaque plastic box to protect the set-up from the light and the temperature evolutions. The imbibition surface was the inferior molded surface of the samples and was put on a capillary geotextile supported by a PVC holder. The ends of the capillary geotextile were immersed in distilled water [19]. The samples mass was measured according to the time with a Sartorius BP211P1 precision scale.

3. RESULTS AND DISCUSSION

3.1. Influence of the biopolymer on samples porosity

Figure 2 presents the results of the capillary imbibition tests carried out with the CEM I and CEM V cement pastes with 3 modes of application:

- painted,
- sprayed,
- used as admixture.

Figure 3 presents the results of the capillary imbibition tests carried out with the CEM I and CEM V mortars with 0, 2.5 and 5% of EPS 180 admixture.

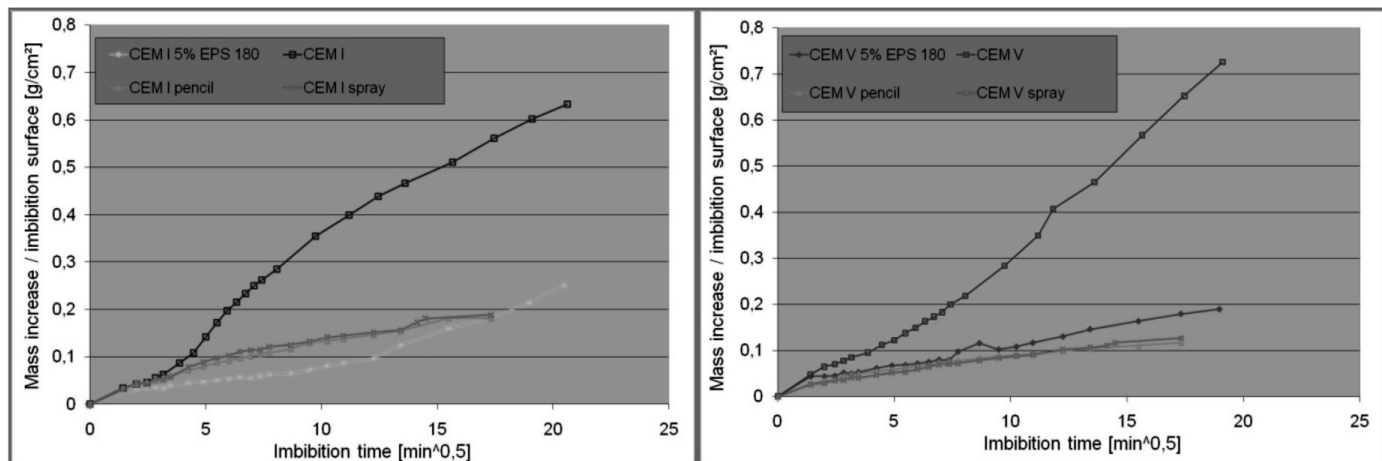


Figure 2: Capillary imbibition tests – mass increase of CEM I and CEM V cement pastes samples

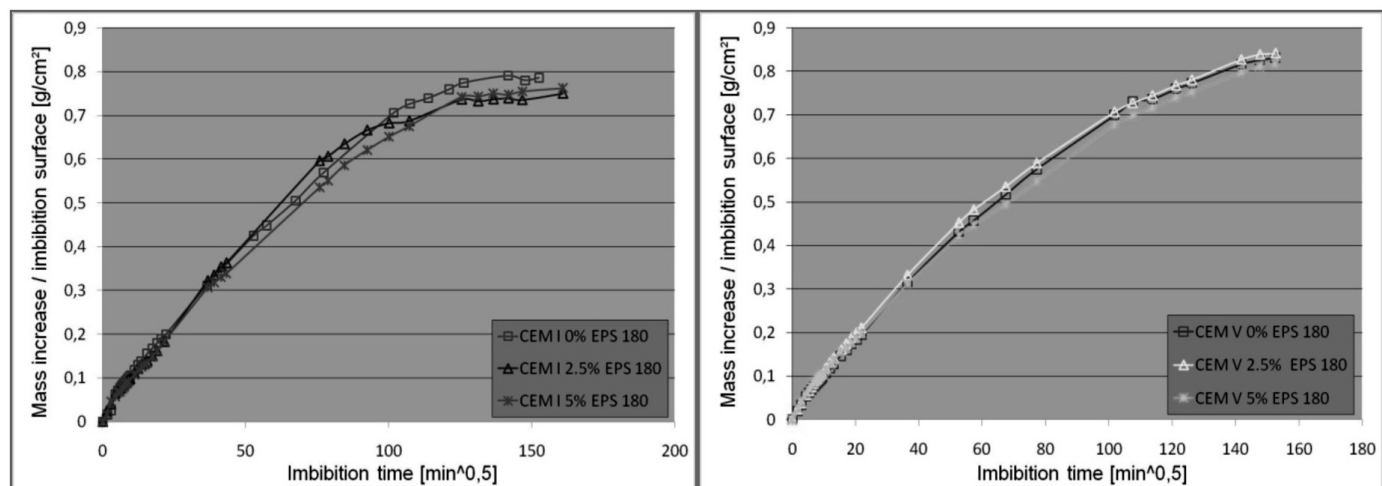


Figure 3: Capillary imbibition tests – mass increase of CEM I and CEM V mortars samples



The behaviour of the cement pastes with the three implementations modes of the EPS 180 solution (admixture, applied in surface by painting or spraying) and without EPS 180 is analyzed. For each cement base, the EPS 180 solution induces an important slow down of the capillary absorption whatever the implementation mode. Compared with reference samples, the EPS 180 solution causes a decrease of the imbibition rate of 68% for CEM I samples after 5 hours of testing and 72% for CEM V containing EPS 180 solution as admixture and finally 83% for the CEM V surface-treated samples. The sample masse increase is linear with the square root time: the absorption of water in the samples is comparable to the absorption of water in a tube and no other physical effect such as the reaction water-cement matrix (*self-sealing effect* [20]) is observed. The influence of cracks, main heterogeneity of the porous structure, was not observed during the capillary fringe rise. The addition of polymers in the cement based material batch is known to influence the hydric transfers inside the hardened material porous network. For example, the superabsorbent polymers [21] interrupt capillary pores, acrylic and styrene-butadiene [22] influence the cement paste porosity clogging the microcracks. In both case, the polymers additions slow down the transfers and transport properties. The EPS 180 solution seems to have the same effect on the transfer properties inside the cement paste porous network.

The results obtained with the mortars samples with EPS 180 admixture (Figure 4) highlight a similar behaviour of all the samples whatever the admixture content for each cement base: the EPS 180 solution has no influence on the water imbibitions kinetics of mortars. The porous structure of cement pastes and mortars are different due to the presence of sand in mortars that induces the formation of the Intergranular Transition Zone (ITZ) [23]. The ITZ correspond to a porosity family of which access diameters are between 0,1 μm and 4 μm [24] and are not found in the cement paste of which pore access diameters are lower than 1 μm and mainly lower than 0,1 μm [25]. The ITZ porosity of mortars is highly connected and offers many penetration ways into the porous network for liquid and aqueous phases [24]. The amount of biopolymer added in the mortars batch is quite low: 5% EPS 180 solution correspond to 66.7 mg of pure ESP 180 per kilogram of cement. This quantity is then high enough to influence the water absorption in cement paste but is too low to modify the imbibition kinetics in mortars.

The embedding depth of the C15 steel rebars is about 6 mm (Figure 1) and the water penetration after 3 hours imbibition test is at least 9 mm for all the cement paste whatever the EPS 180 admixture content. After one-week immersion, the seawater then reached the rebars embedded in cement paste. The EPS 180 are effectively able to clog the cement paste porous network and then to decrease its capillary imbibition rate, but, after one week, the clogging cannot forbid seawater to reach the rebars. The modification of the electrochemical behavior of the rebars embedded in cement paste containing EPS 180 is due to the modifications of the steel-cement paste interface.

3.2. Influence of biopolymer as admixture on corrosion resistance of steel rebars

Table 2 presents the OCP values for the C15 low-carbon steel rebars embedded in the CEM I and CEM V cement pastes with different proportions of admixture.

EPS 180 admixture content	0%	0,5%	1%	2,5%
CEM I - OCP [V/Electrode Ag-AgCl]	-0,148	-0,069	-0,178	-0,193
CEM V - OCP [V/Electrode Ag-AgCl]	-0,554	-0,467	-0,456	-0,433

Table 2: C15 steel rebars OCP, CEM I and CEM V cement pastes

Figures 4 and 5 present the Nyquist plot of the EIS results for the C15 steel rebars embedded in CEM I and CEM V cement pastes with different proportions of admixture.

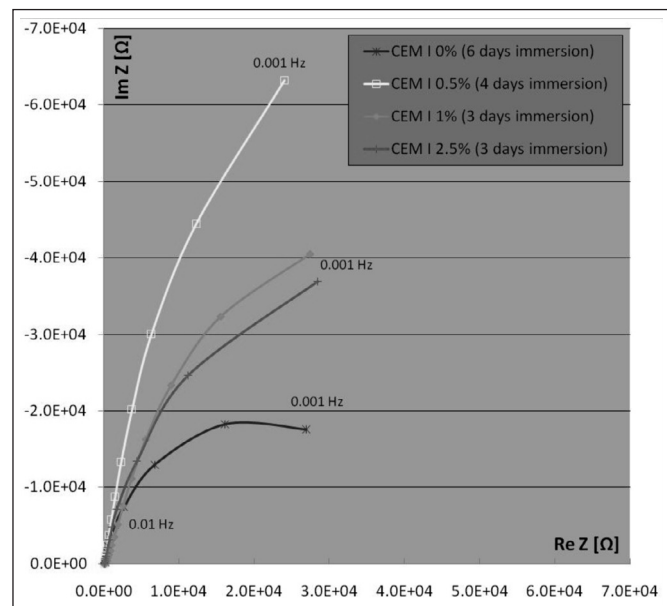


Figure 4: Nyquist plot of the EIS results – CEM I reinforced cement pastes samples

The impedance of the electrolyte and of the embedding cement paste is modeled by an electrolyte resistance R_e . At corrosion potential (OCP), the current is equal to zero and the cathodic impedance is parallel to the anodic one. The anodic impedance corresponds to the rebars passive layer and can be modeled by a Constant Phase Element (CPE) defined by two parameters Q and α [26]. The parameter is linked to the passive layer heterogeneity at different level (surface roughness, etc.) and Q corresponds to the differential capacitance when α is equal to 1. The cathodic impedance corresponds to the oxygen reduction reaction and is modeled by a charge transfer resistance R_{tc} . Figure 6 presents the equivalent circuit and the table 3 presents the values of its components calculated thank to the fitting software Zview.

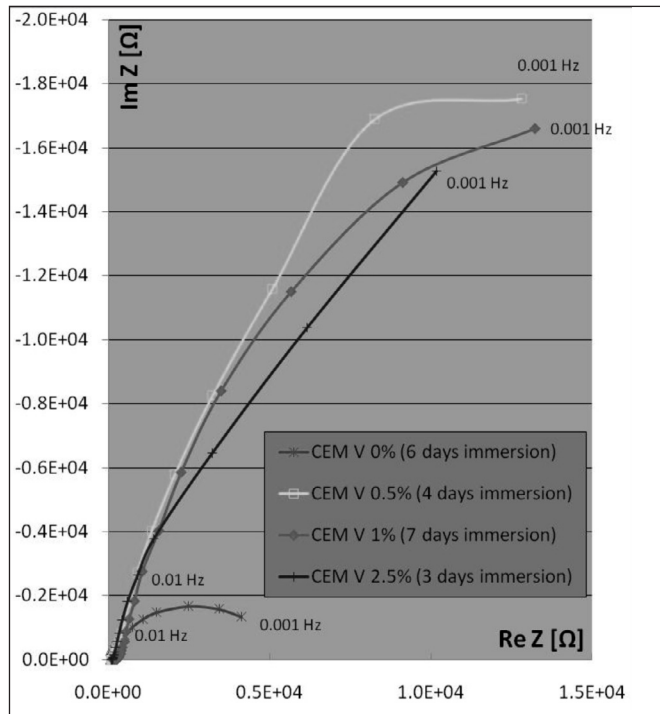


Figure 5: Nyquist plot of the EIS results – CEM V reinforced cement pastes samples

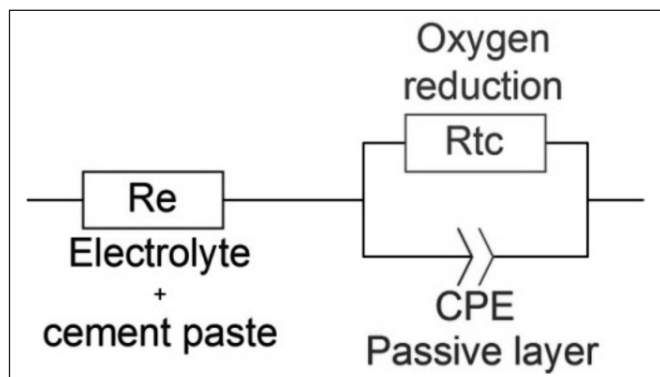


Figure 6: EIS tests - equivalent circuit

The stabilized corrosion potential of the C15 low-carbon steel immersed in the natural seawater is -0,630 V/ECS that is coherent with the -0.7V/ECS value for mild steel in seawater given in the literature [27]. The interstitial solution of sound cement based materials is resulting of the mixing water and the dissolution of cement grains. The composition of this solution depends on the cement composition (clinker, blast furnace slag, siliceous fly ashes) and mainly contains Ca^{2+} , Na^+ , K^+ , OH^- and SO_4^{2-} ions [28]. When carbon steel is embedded in such materials, the chemical composition and the pH about 13.5 of the interstitial solution leads to the formation of a passive layer at rebars surface. This passive layer is mainly composed by iron hydroxide ($Fe(OH)_2$) and calcium hydroxide ($Ca(OH)_2$) and influences the rebars OCP [29, 30]. It is then not surprising that the OCP of the rebars embedded in cement paste without EPS 180 admixture goes up: + 440 mV for the CEM I and + 40 mV for the CEM V. When EPS 180 admixture is added, there is no notable evolution of the rebars OCP: from - 50 mV up to + 80 mV for the CEM I and from + 90 mV up to + 110 mV for the CEM V.

The analysis of the EIS results highlights that the CPE parameters values (Q , α) for each cement base samples are quite close whatever the EPS 80 admixture content. However the CPE parameters values are different for the two cement bases. These results show that the cement chemistry influences the composition of the passive layer more than the EPS 180 admixture content.

The EPS 180 induces a significant increase of the R_{tc} values. Compared with the samples without EPS 180 admixture, R_{tc} values are multiplied by factors between 2.36 and 7.75 for samples CEM I with EPS 180 and between 8.5 and 12.31 for those of CEM V. The decrease of the cathodic reaction kinetics is observed for all EPS content including the lowest concentration of EPS 180 admixture (0.5%).

Samples	Re [Ω]	R_{tc} [$k\Omega$]	Q [$s^\alpha \cdot \Omega^{-1} \cdot cm^{-2}$]	α
C15 rebars in CEM I 0%	1 050	553	0,000 14	0,86
C15 rebars in CEM I 0,5%	870	4 284	0,000 13	0,89
C15 rebars in CEM I 1%	2 200	2 476	0,000 11	0,79
C15 rebars in CEM I 2,5%	870	1 305	0,000 15	0,87
C15 rebars in CEM I 5%	1 240	13 300	0,000 11	0,85
C15 rebars in CEM V 0%	660	58,4	0,000 32	0,76
C15 rebars in CEM V 0,5%	1 690	719	0,000 23	0,815
C15 rebars in CEM V 1%	3 100	616	0,000 23	0,785
C15 rebars in CEM V 2,5%	1 270	497	0,000 25	0,83

Table 3: Equivalent circuit parameters



4. CONCLUSION

After the samples immersion in natural seawater, the EPS 180 biopolymer admixture added in reinforced CEM I and CEM V cement pastes induces the modification of the cathodic reaction of the C15 low-carbon steel rebars. This admixture also modifies the porous network of the cement paste that is highlighted by a slowdown of the capillary imbibition kinetics, this phenomenon is not observed for the mortars. The corrosion inhibition is then essentially influenced by the modification of the cement paste – steel interface rather than by the clogging of the porous network. This new admixture inhibits the corrosion of low carbon-steel rebars in CEM I and CEM V cement paste samples. These first results confirm that the use of ecofriendly biopolymer admixtures could be an alternative to classical corrosion inhibiting treatment for the reinforced concrete in natural environment. The aim is to contribute to the effort in sustainable development thanks to the microorganisms (*Lactobacillus reuteri* bacteria) allowing the production of more eco-friendly concrete.

5. ACKNOWLEDGEMENT

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