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ORIGINAL PAPER

Tolerance limit of chloride for steel in blended cement mortar using the cyclic polarisation technique

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Abstract The tolerance limit for chloride in ordinary Portland cement (OPC) and blended cements such as Portland pozzolana cement (PPC) and Portland slag cement (PSC) was assessed by cyclic polarisation. This study covers both cement extracts and mortar. The salient features of this investigation were: in extracts, the tolerance limit for chloride actually doubles for PSC when compared to PPC and OPC. The tolerance limit for chloride for various mortars follows the order: PSC > PPC > OPC. In OPC and PPC mortar, the repassivation potential (E_{rep}) shifted negatively with higher amounts of free chloride but in PSC mortar E_{rep} shifted positively (+590 mV) even in the presence of 5,000 ppm of free chloride. PSC takes longer time (50 days) to reach E_{rep} indicating perfect passivity maintained for the embedded steel.

Keywords Chloride corrosion · Blended cement · Rebar corrosion · Concrete

Abbreviations

OPC	Ordinary Portland cement
PPC	Portland pozzolana cement
PSC	Portland slag cement
OCP	Open circuit potential
TMT	Thermomechanically treated
SCE	Saturated calomel electrode
E_{rep}	Repassivation potential

1 Introduction

Chloride-induced corrosion of reinforcing steel is recognized as a primary factor contributing to the deterioration of concrete structures at the steel/concrete interface. Once the chloride content exceeds the tolerance limit, initiation of rebar corrosion occurs. This tolerance limit for chloride for OPC concrete has been studied in the laboratory as well as in the field conditions. Nowadays blended cements are extensively used in most important concrete structures due to cost saving, energy saving and consideration of resources.

Free chlorides are mainly responsible for rebar corrosion [1]. If the free chloride to hydroxide ratio exceeds 0.6, loss of passivity occurs and pitting progresses. The presence of free chloride not only alters the Pourbaix equilibrium diagram (it reduces the area of the passive region as shown in Fig. 1, but also transfers the rebar from the passive to the active region) [2].

The corrosion reactions can be represented as follows [3, 4].

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \qquad (1)$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^{-} \rightarrow 4\mathrm{OH}^{-} \qquad (2)$$

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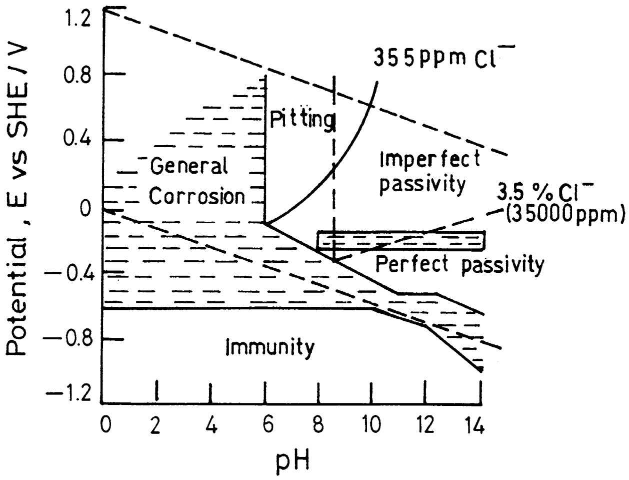

Fig. 1 Influence of chloride on corrosion and passivation of iron

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow \text{White corrosion product} \tag{3}$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \rightarrow \text{Red rust} \tag{4}$$

$$3Fe + 8OH^- \rightarrow Fe_3O_4 + 4H_2O + 8e^- \rightarrow \text{Black rust} \tag{5}$$

At high chloride concentrations,

$$Fe + 2Cl^- \rightarrow FeCl_2 \rightarrow Fe^{++} + 2Cl^- + 2e^- \rightarrow \text{Yellowish green} \tag{6}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{7}$$

$$6FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ + 12Cl^- \tag{8}$$

The reaction between iron and free chloride is self-perpetuating in that the free chloride originally responsible for the reaction is released for re-use when iron hydroxide is formed. In fact, the free chloride acts as a reaction catalyst [5]. Even though a high level of alkalinity remains around the steel embedded in concrete, the chloride ions can locally depassivate the steel and promote rebar corrosion.

1.1 Expression of "threshold value"

Corrosion begins when a certain chloride concentration has been reached around the steel. This concentration is called the tolerance limit for chloride or chloride threshold level [6]. Normally, in concrete core sample analysis in the laboratory, chloride content is expressed as a percentage on the basis of the weight of cement because cement constituents like calcium oxide and aluminium oxide play a major role in converting chloride from the free state to the complex state. In contrast, in the case of core samples collected from bridges and structures, chloride content is expressed as a percentage on the basis of the weight of concrete as it is very difficult to find the cement content in existing structures. But from a corrosion point of view, only the free chloride content is responsible for inducing rebar corrosion. In estimating the chloride content in concrete core samples, only the chloride content at the steel/concrete interface plays a major role in inducing passivity. But it is also very difficult to estimate the chloride content at the steel/concrete interface. Microelectrodes should be developed on the basis of ion selective electrodes to estimate the chloride content at the steel/concrete interface, because this interface plays a major role in identifying the active/passive condition of steel rebars. A literature survey carried out on the threshold limit for chloride to induce rebar corrosion in bridges and concrete structures revealed that various factors in the design stage itself, as well as during prolonged exposure, influence the quantity of chloride required to destroy passivity and induce rebar corrosion [7]. The role of chloride in inducing reinforcement corrosion has been extensively studied [8–10]. In addition to chloride content, alkalinity and oxygen contents also play a major role in rebar corrosion [11]. The effect of cement types on corrosion resistance of steel has also studied [12, 13]. The chloride threshold limit for reinforcement corrosion was studied by laser induced breakdown spectroscopy [14], X-ray fluorescence [15], and mathematical modelling methods [16, 17]. The critical threshold chloride level for corrosion of steel in concrete was reviewed recently [18]. The minimum amount of chloride ions to initiate a single pit has been investigated as a function of the iron potential and the pH of the electrolytic solution [19]. The threshold limit for chloride is considerably reduced with 10% silica fume blended concrete [20]. Potentiostatic tests are found to be an appropriate method to determine the threshold limit for chloride for depassivation of reinforcements [21]. The objective of the present investigation is to study the influence of various cements such as ordinary Portland cement (OPC), Portland pozzolana cement (PPC) and Portland slag cement on the tolerance limit for chloride towards reinforcement corrosion in cement extracts and mortars using cyclic polarisation.

2 Experimental details

2.1 Cement

Ordinary Portland cement (IS: 12269-87), Portland pozzolana cement (IS: 1489-1991) Part-1 and Portland slag cement (IS: 455-1989) were used throughout this investigation. The chemical composition of OPC, PPC and PSC are given in Table 1.

Table 1 Composition of OPC, PPC and PSC cements

Constituents	Wt.%		
	OPC	PPC	PSC
SiO_2	20–21	28–32	26–30
Al_2O_3	5.2–5.6	5.0–8.0	9.0–11.0
Fe_2O_3	4.4–4.8	4.9–6.0	2.5–3.0
CaO	62–63	43–45	44–46
MgO	0.5–0.7	1.0–2.0	3.5–4.0
SO_3	2.4–2.8	2.4–2.8	2.0–2.4
LOI	1.5–2.5	3.0–3.5	1.5–2.5

2.2 Preparation of cement extracts

Cement was sieved through 90-µm sieve and extracts were prepared as follows. To 100 g of the cement, 100 mL of distilled water was added and shaken vigorously using a Microid flask mechanical shaker for about 1 h. The extracts were then collected by filtration. The pHs of OPC, PPC and PSC extracts were 12.76, 12.35 and 12.54, respectively. The initial chloride level for the various extracts was found to be 20–25 ppm.

2.3 Cyclic polarisation test

Cyclic polarisation studies were carried out using a conventional three electrode cell. Both anodic and cathodic polarisation curves were recorded potentiodynamically using an ACM instrument (UK). The potentiodynamic condition corresponds to a potential sweep rate of 60 mV min^{-1} and potential ranges of 0 to +1,000 mV. All the experiments were carried out at room temperature of 35 ± 1 °C.

2.3.1 Studies in cement extracts

In the first set of experiments, cyclic polarisation was carried out in cement extracts (OPC, PPC and PSC) containing various concentrations of chloride. Thermomechanically treated (TMT) rebar with an exposed cross sectional area of 1 cm^2 moulded in Araldite acted as working electrode. The electrode was given fine mechanical polishing followed by polishing with emery papers (0/0 to 4/0 grades) and then degreased with acetone. Saturated Calomel Electrode (SCE) and platinum foil as reference and counter electrodes, respectively, were used. Test solution (200 mL) was placed in the cell and stirred using a magnetic stirrer to minimise concentration polarisation effects. Time intervals of 10–15 min were allowed for each system to attain steady state and the open circuit potential (OCP) was noted.

2.3.2 Studies in cement mortar

In the second set of experiments, cylindrical mortar pieces (1:2) of size (20 mm diam., 20 mm height) with OPC, PPC and PSC were cast with TMT rod of 12 mm diam. and height 10 mm embedded in the centre of the mortar. After 24 h of casting, specimens were cured in Millipore water for 28 days. After 28 days, the mortars were immersed in 1%, 2% and 3% chloride solutions. Cyclic polarisation tests were carried out daily for all the systems until the critical chloride level reached the steel. Experiments were terminated when E_{rep} was noted for the individual system.

2.4 Visual observations

During cyclic polarisation in cement extracts the TMT steel specimens were carefully examined for corrosion products. In cement mortars, at the end, specimens were removed from the solutions, washed with water, broken open and the pitting of steel was examined visually.

2.5 Preparation of extracts from cement mortar for chemical analysis

The mortar specimens were crushed and sieved through a 90-µm sieve. A known quantity of the sieved powder and triple-distilled water was mixed and shaken for 1 h using a microid mechanical shaker. It was then filtered through a Whatman filter paper. The filtrate was then used for chloride determination and the titration was carried out as per the procedure given below.

Five millilitres of filtrate was taken and one drop of phenolphthalein indicator was added. A pink-coloured solution was obtained. This shows that the pH of the solution was alkaline. This was then neutralized with 0.05 M sulphuric acid by decolourising the pink colour. Then a few drops of 10% potassium chromate indicator were added and the solution was titrated against 0.1 M silver nitrate solution. The end point was the appearance of a yellowish red colour. The titration was repeated until reproducible values were obtained. Free chloride was estimated for extracts obtained from OPC, PPC and PSC mortars.

The pH of the pore solution was also determined. The pH of the filtrate was measured using a portable Istek Inc. (Model 76 P) pH meter. The pH meter was calibrated using a standard buffer solution of pH 9. Minimum of three readings were taken for each system and the average pH value was recorded.

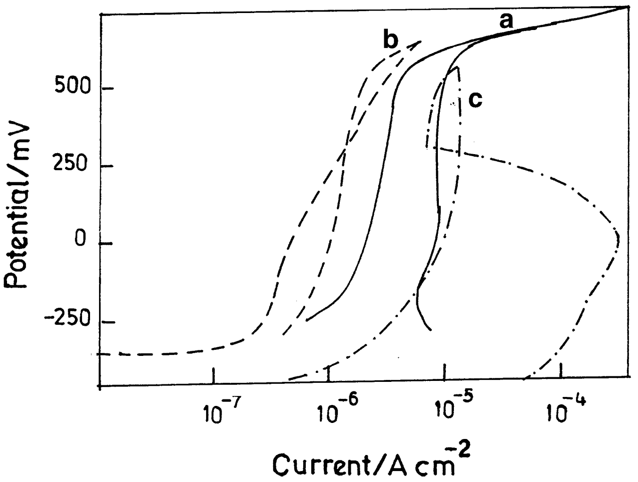

Fig. 2 Cyclic polarisation curves for steel in cement extracts. (**a**) OPC (900 ppm Cl^-), (**b**) PPC (900 ppm Cl^-) and (**c**) PSC (2000 ppm Cl^-)

3 Results and discussion

Figure 2 shows the cyclic polarisation curves for TMT steel in OPC, PPC and PSC extracts.

3.1 Cyclic polarisation of steel in OPC extract

The data from cyclic polarisation curves for steel in OPC extract are reported in Table 2. The tolerance limit for chloride was found to be 800 ppm. At 900 ppm pitting corrosion initiated. E_{rep} was observed at +600 mV versus SCE. As the chloride concentration increased, the OCP of steel in OPC extract also increased negatively.

Table 2 Cyclic polarisation parameters for steel in OPC, PPC and PSC cement extracts with different concentration of chlorides

System	Chloride level (ppm)	OCP (mV) versus SCE	E_{rep} (mV) versus SCE	Visual observation
OPC	500	−385	–	No pitting
	800	−390	–	No pitting
	900	−392	600	Pitting
PPC	500	−341	–	No pitting
	800	−357	–	No pitting
	900	−359	250	Pitting
PSC	500	−430	–	No pitting
	800	−433	–	No pitting
	900	−454	–	No pitting
	1,000	−445	–	No pitting
	1,500	−466	–	No pitting
	1,700	−471	–	No pitting
	1,800	−482	–	No pitting
	1,900	−484	–	No pitting
	2,000	−489	250	Pitting

3.2 Cyclic polarisation of steel in PPC extract

The data from cyclic polarisation curves for steel in PPC extract are reported in Table 2. The tolerance limit for chloride was found to be 800 ppm. At 900 ppm, pitting corrosion initiated. E_{rep} was observed at +250 mV versus SCE. As the chloride concentration increased, the OCP of steel in PPC extract also increased negatively. The tolerance limit for chloride for steel in both OPC and PPC extracts were found to be <900 ppm.

3.3 Cyclic polarisation of steel in PSC extract

The data from cyclic polarisation curves for steel in PSC extract are reported in Table 2. The tolerance limit for chloride was found to be 1,900 ppm. At 2,000 ppm, pitting corrosion initiated. E_{rep} was observed at +250 mV versus SCE. As the chloride concentration increased, the OCP of steel in PSC extract also increased negatively. Even though the E_{rep} is observed to be the same as that of PPC extract, the tolerance limit for chloride actually doubled for PSC extract. The tolerance limit for chloride for various cements follows the order: PSC > PPC and OPC.

The better performance of PSC is due to the presence of more aluminate content, which is responsible for converting the free chloride ions into the complex form.

3.4 Cyclic polarisation of rebar in OPC mortar

Cyclic polarisation curves for rebar in OPC mortar exposed to 1%, 2% and 3% NaCl solution are given in Fig. 3 and data are summarized in Table 3. E_{rep} shifted negatively as the chloride content increased. The amount of chloride permeated also increased as the chloride concentration increased from 1% to 3% NaCl. E_{rep} were observed after

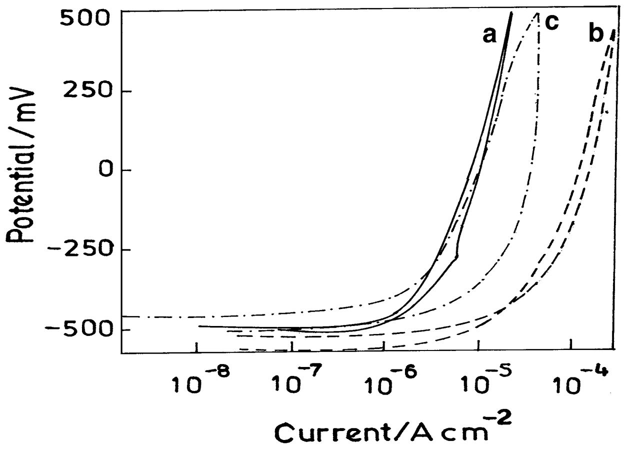

Fig. 3 Cyclic polarisation curves for rebar in OPC mortar. (**a**) 1% Cl^-, (**b**) 2% Cl^- and (**c**) 3% Cl^-

Table 3 Cyclic polarisation parameters for rebar in OPC, PPC and PSC mortar exposed to different concentration of chlorides

System	Chloride level (%)	OCP (mV) versus SCE	E_{rep} (mV) versus SCE	Time taken for E_{rep} (Days)	Free Cl$^-$ contents (%)
OPC	1	−507	−300	30	2,850
	2	−562	−465	24	4,960
	3	−512	−475	24	8,640
PPC	1	−569	−70	77	2,800
	2	−517	−400	42	4,650
	3	−568	−440	42	6,600
PSC	1	−640	−210	79	1,800
	2	−522	−435	50	3,960
	3	−509	+590	50	5,000

30, 24 and 24 days for 1%, 2% and 3% NaCl solutions, respectively.

3.5 Cyclic polarisation of rebar in PPC mortar

Cyclic polarisation curves for rebar in PPC mortar exposed to 1%, 2% and 3% NaCl solution are given in Fig. 4 and data are summarized in Table 3. E_{rep} shifted negatively as the chloride content increased. The amount of chloride permeated also increased as the chloride concentration increased from 1% to 3% NaCl. E_{rep} were observed after 77, 42 and 42 days for 1%, 2% and 3% NaCl solutions, respectively.

The time taken to reach E_{rep} increased by 2.5 times in 1% NaCl, 1.75 times in 2% NaCl and 1.75 times in 3% NaCl when compared to OPC mortar. For example at 3% NaCl solution, the time taken to reach E_{rep} for OPC and PPC mortar was found to be 24 and 42 days, respectively. These data clearly proved the pore filling effect and pore structure refinement of PPC which reduced the permeability of chloride and hence increased the time taken to reach E_{rep}. The improvement in the permeability characteristics of PPC is due to the main hydration reaction as follows:

In the OPC and PPC systems, the primary hydration reaction is

$$2(3\mathrm{CaO}\cdot\mathrm{SiO_2}) + 6\mathrm{H_2O} \rightarrow 3\mathrm{CaO}\cdot 2\mathrm{SiO_2}\cdot 3\mathrm{H_2O} + 3\mathrm{Ca(OH)_2} \quad (9)$$

But in the PPC system, the additional secondary hydration reaction is

$$3\mathrm{Ca(OH)_2} + 2\mathrm{SiO_2} + \mathrm{H_2O} \rightarrow 3\mathrm{CaO}\cdot 2\mathrm{SiO_2}\cdot 3\mathrm{H_2O} \quad (10)$$

In the PPC system, the $\mathrm{Ca(OH)_2}$ content reduction is due to the secondary hydration reaction. During hydration, in PPC, $\mathrm{Ca(OH)_2}$ is consumed but in OPC, $\mathrm{Ca(OH)_2}$ is produced. This is the main advantage of using PPC cements to decrease the permeability of the concrete and thereby increase the corrosion resistance.

3.6 Cyclic polarisation of rebar in PSC mortar

Cyclic polarisation curves for rebar in PSC mortar exposed to 1%, 2% and 3% NaCl solution are given in Fig. 5 and

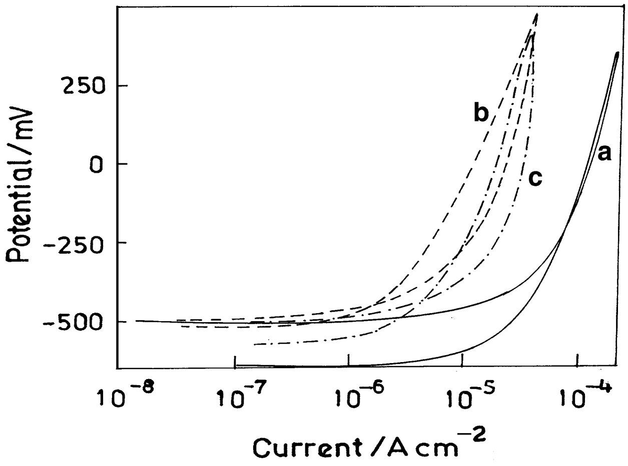

Fig. 4 Cyclic polarisation curves for rebar in PPC mortar. (**a**) 1% Cl$^-$. (**b**) 2% Cl$^-$ and (**c**) 3% Cl$^-$

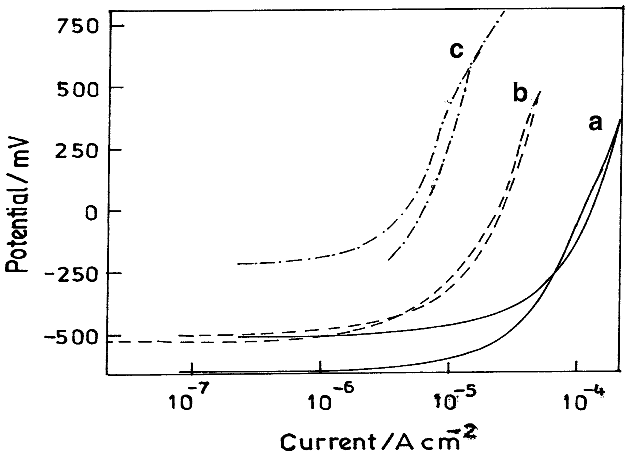

Fig. 5 Cyclic polarisation curves for rebar in PSC mortar. (**a**) 1% Cl$^-$. (**b**) 2% Cl$^-$ and (c) 3% Cl$^-$

data are summarized in Table 3. E_{rep} shifted negatively as the chloride content increased. The amount of chloride permeated also increased as the chloride concentration increased from 1% to 3% NaCl. E_{rep} were observed after 79, 50 and 50 days for 1%, 2% and 3% solutions, respectively. In the case of PSC mortar E_{rep} shifted positively for 3% NaCl solution (+590 mV versus SCE) and also the time taken to reach E_{rep} was doubled when compared to OPC mortar.

The better performance of PSC is due to the aluminate phase binding the chlorides into complex forms. Fixing of chloride in concrete by the formation of complex aluminate phases has been reported previously [22]. About 50–80% of chloride ions are bound by aluminate phases by the action of calcium oxide and aluminate with chloride, forming calcium chloro-aluminate complexes ($CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$).

The mechanism of formation of the complex Friedel salt is by a precipitation method. Friedel's salt consists of two principal $[Ca_2Al(OH)_6 \cdot 2H_2O]^+$ layers that require a balancing negative charge for stability. The availability of Cl^- (from dissolved NaCl) satisfies charge neutrality in the solid but this disturbs the ionic charge balance in the pore solution. To compensate for this however, an equivalent amount of Na^+ ions would be required to leave the pore solution, i.e., be absorbed into solid phases.

3.7 Free chloride contents

At potentials more noble the E_{rep}, the medium has a greater tendency to repassivate the steel even in the presence of higher amounts of chloride. In OPC and PPC mortar, E_{rep} shifted negatively. This is due to the higher amount of free chlorides available in mortar. For example, in PPC mortar −70 and −440 mV were measured as E_{rep} as the free chloride increased from 2,800 to 6,600 ppm, respectively. On the other hand, in the case of PSC mortar, even though 5,000 ppm of free chloride is available to induce passivity breakdown, E_{rep} is observed to be +590 mV indicating perfect passivity maintained for the embedded steel. This observation is also confirmed by the longer time (50 days) to reach E_{rep}. The pHs of the pore solution were 11.90, 12.00 and 12.34, respectively, for OPC, PPC and PSC. Here the alkalinity was considerably reduced for the OPC system. PSC and PPC maintained their alkalinity even with the higher amount of chlorides.

4 Conclusions

The following conclusions can be drawn:

- In cement extracts, even though E_{rep} is observed to be the same for both PPC and PSC systems, the tolerance limit for chloride is doubled for PSC.
- The tolerance limit for chloride is enhanced due to the chloride binding capacity of PSC.
- In mortar, the time taken to reach E_{rep} of rebar is more or less the same for both PPC and PSC mortar (actually doubled when compared to OPC). E_{rep} shifted positively for rebar in PSC mortar indicating perfect passivity maintained for the embedded steel.
- In OPC and PPC mortar E_{rep} shifted negatively with higher amounts of free chloride but, in PSC mortar, E_{rep} shifted positively (+590 mV), even in the presence of 5,000 ppm of free chloride. This observation is also confirmed by the longer time (50 days) to reach E_{rep}.

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