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First steps in developing cement-based batteries to power cathodic protection of embedded steel in concrete



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Abstract

This paper presents the first steps in developing innovative cement-based batteries to power cathodic protection in reinforced concrete structures. Initial electrical outputs of 1.55V and 23mA have been found to be sufficient to polarise prescribed corrosion currents of 20mA per m² of embedded steel. Cathodic protection is a well-developed and powerful technique to limit the effects of steel reinforcement corrosion.

However, as it requires an electrical supply day and night, it is often powered by non-environmentally friendly diesel generators or connected to the electrical grid. This paper focuses on increasing the ionic conductivity of the solution in the cement pores, increasing the porosity of the cement, examining ways of sealing moisture into the cement and comparing different electrode materials and treatments. The batteries presented consist of different combinations of Portland cement, water, carbon black and salt solutions with embedded copper acting as the cathode and magnesium, aluminium or zinc cast as the anode.

The preliminary findings demonstrate that cement-based batteries can produce sufficient sustainable electrical outputs with the correct materials and arrangement of cast-in anodes. Work is ongoing to determine how these batteries can be recharged using photovoltaics which will further enhance their sustainability properties.

Key Words:

Cement-based batteries; electrolyte; pore conductivity; concrete; corrosion; cathodic protection.

Glossary:

Impressed current cathodic protection (ICCP).

1. Introduction

Cement could be considered as green as it is a rock-based material, ground into a fine powder and mixed with other raw components. However, as a result of the rock extraction and mixing, its green credentials are somewhat lost. Therefore, sustainability discourse related to cement primarily focuses on efforts to make it more environmentally friendly over its whole life to diminish the CO₂ released during its production.

However, cement-based products such as concrete can facilitate energy efficiency in the finished structure. This includes the harnessing of concrete's thermal mass to reduce heating and cooling needs for buildings by absorbing heat (daytime solar gains or when indoor heating system is turned on), storage and later release (at night through the release of these solar gains).

A lot of work is ongoing to reduce the environmental impact of cement-based materials while still maintaining performance (Nanukuttan *et al*, 2010; EN206, 2000). This includes replacing cement with supplementary cementitious materials such as ground granulated blastfurnace slag and pulverised fuel ash. Other areas of research consider the replacement of natural aggregates in concrete with materials that would otherwise be landfilled, including crumb-rubber (Holmes *et al*, 2014) and bottom ash (Sandhya *et al*, 2013).

This paper presents the first steps in developing novel cement-based batteries designed to power low-energy cathodic protection. One example is Impressed Current Cathodic Protection (ICCP) of reinforcement in concrete structures. ICCP protects reinforcing steel from corrosion by connecting it to an inert, less noble, metal and passing low-level current through it using an external power source (Polder, 1998).

2. Background

In a battery, ions move through the electrolyte and electrons move through the circuit from the anode to the cathode (see Figure 1). Conventional alkaline batteries use zinc as the anode, manganese dioxide compact as the cathode and salt solution as the electrolyte, with all components held together in a sealed container.

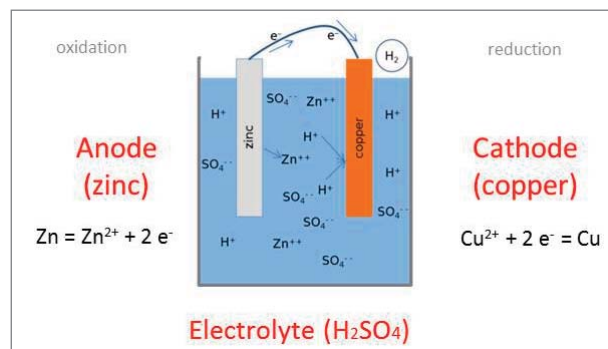


Figure 1: Conventional battery arrangement.

The electrolyte in a battery is an ionic conductor but also an electronic insulator which resists the movement of electrons. The ionic conductivity of the electrolyte should be high with a low electrical resistance, thus allowing the battery to carry high current (Meng and Chung, 2010). Liquid electrolytes traditionally perform better in batteries due to the high mobility of ions with a continuous interface between electrodes and electrolyte. Examples of solid electrolytes are polymers or ceramics doped with ions to improve ion movement.

The process of embedded steel corrosion in concrete is an example of ionic flow through hardened concrete. During corrosion, iron atoms are removed from the steel surface by electrochemical reaction. These atoms then dissolve into the surrounding electrolyte solution which, in concrete, can only occur where pores exist at the steel anodic site. Electrons must therefore transfer from this anodic site to a cathodic area, which develops a surplus of electrons. The transfer of electrons occurs along the metal and creates a current between areas of differing potential. The ions from the reactions, such as the ferrous ion (Fe^{2+}), pass into the solution trapped in the concrete pores and meet with hydroxyl ions (OH^-) to form ferric hydroxide which further reacts to form rust as shown in Figure 2.

Meng and Chung (2010) provided the initial proof of concept that cement-based batteries could be designed to supply a voltage and current.

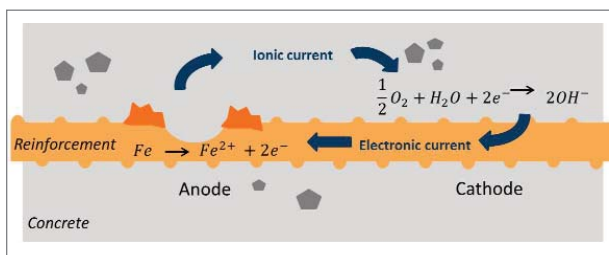


Figure 2: Corrosion process in embedded steel in concrete.

In their layered design the cathode was a mix of manganese dioxide particles and cement, the electrolyte consisted of cement and the anode contained cement and zinc particles (see Figure 3).

The advantage of this design over electrode (non-cement-based) probes is that the active phase in both anode (zinc) and cathode (manganese dioxide) are in direct contact with the electrolyte (pore solution in the cement paste) in the anodic and cathodic layers and not just at the interface with the electrolyte (Meng & Chung, 2010). The outputs from this type of battery design were very low. Open-circuit voltages of up to 0.72V and current up to 120 μA (current density 3.8 $\mu\text{A}/\text{cm}^2$) were recorded and only operated when saturated.

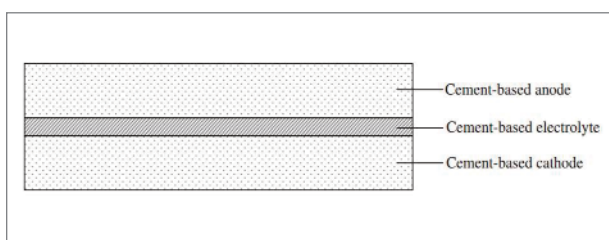


Figure 3: Layered cement-based battery (Meng and Chung, 2010).

Rampradheep *et al* (2012) used similar constituents in a layered battery to produce a maximum voltage of 0.6V and an undisclosed current. Cement-batteries cast with carbon fibers and carbon nanotubes in the electrolyte layers (Qiao *et al*, 2014) yielded maximum power outputs of 0.7V and 35.21 $\mu\text{A}/\text{cm}^2$.

There is little published research into the possibility of using batteries for generating low-level electrical power for use in ICCP and none, at the time of writing at least, on using cement-based batteries. As this area is so lightly researched there have not been many advances in making these batteries more efficient, powerful, longer-lasting and rechargeable.

A seawater battery to incorporate cement between the magnesium and carbon probes and maintained in a seawater bath has been reported (Ouellette & Todd, 2014) as a corrosion-based energy harvester. Adding the cement passively limited the amount of consumable oxygen rather than a functioning electrolyte system. As discussed previously, corrosion of reinforcement in concrete creates differing potentials in the steel and induces a current to flow. This corrosion energy can be harvested and used for corrosion sensors (Ouellette and Todd, 2014; Qiao *et al*, 2011).

3. Methodology

The design considerations for the cement-based battery developed here are outlined below. Firstly, increasing the ionic conductivity of the cement electrolyte will improve the performance. For this, water-soluble salts such as Epsom, Alum and sodium chloride are investigated in solution and as solid granules.

The electrically active additive carbon black enhances the connectivity between electrodes. This is particularly true for the cathode which may use an electrochemically non-conductive material such as manganese dioxide (Meng and Chung, 2010). The volume of carbon black added should be high enough to aid electronic connectivity but not so high as to reduce the proportion of the cathode and anode.

For conductive materials such as zinc (which forms electrically non-conductive zinc oxide on its surface), thin reaction products can impede the output of the battery as they reduce the interface between the electrodes and electrolyte. Such layers can be removed by washing with acetic acid and rinsing with a volatile liquid such as ethanol prior to adding to the mix.

Both the anodes and cathodes need to be electrical conductors. The anode is the more active of the two as it undergoes chemical oxidation during discharge and will be lost over time, thereby losing electrons. The cathode is nobler than the anode and remains more stable during discharge as it gains electrons.

As a battery discharges its internal resistance increases as the electrolyte becomes less conductive. Its open circuit voltage decreases as chemicals become more dilute. The results here present the current and voltage under load.

Layered battery

The first cement-based battery cast is shown in Figure 4 and was based on the work by Meng and Chung (2010). However, the mix

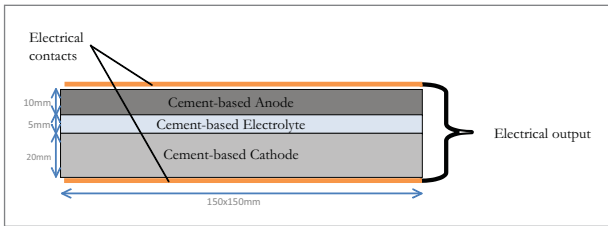


Figure 4: Layered battery schematic.



(a) Layered cement-based battery



(b) Batteries stored in water and Epsom salt



(c) Electrical contacts (conductive copper)

Figure 5: Layered batteries cast.

resulted in an unworkably-dry paste for the electrode layers which crumbled when set. The electrolyte layer was too wet and sandwiched out of the mix when the top layer was placed. The proportions of the mix are shown in Table 1. The zinc powder was washed with acetic acid to remove any dirt or oxide layers and rinsed with ethanol to remove the acid prior to mixing.

The surface of the moulds was oiled and the dry components were mixed together before adding the water-reducer and water. The addition of carbon black in the electrode layers made the mix difficult to manipulate and it had to be kneaded to ensure

Table 1 – Mix proportions used - layered battery

Cathode	MnO ₂	218
	Water reducer	11
	Distilled water	22
	Carbon black	15
Electrolyte	Cement	88
	Water reducer	4
	Distilled water	18
Anode	Cement	282
	Zn	84
	Water reducer	5
	Distilled water	91
	Carbon black	7

adequate mixing before being pressed into the mould. The cathode layer was placed first, followed by a single ply of tissue to prevent drying shrinkage cracks and to ensure the separation of the layers.

The electrolyte layer followed (also covered with a tissue) and finally the anode was applied, which was levelled using a trowel. The battery was left to cure in the mould for 24 hours under damp hessian and polythene sheets. After removal from the mould, readings for open-circuit voltage and resistor load current were taken using a multimeter. This battery is shown in Figure 5a.

Four batteries were made using this design. Two were placed in distilled water to cure for a further 48 hours after removal from the mould (Figure 5b). The other two were placed in a 0.5M solution of Epsom salt (MgSO₄·7H₂O) for 48hrs (Figure 5b).

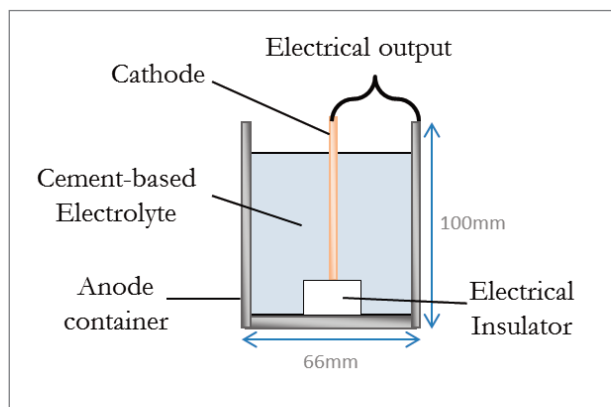


Figure 6: Battery housed in a metal can.

One Epsom salt battery and one distilled water battery were sealed with Sikagard 680S protective coating to maintain the internal moisture content. Electrical contacts were made using conductive copper tape as shown in Figure 5c.

Cement-based batteries housed in a can

Cement batteries in this form (Figure 6) were not identified in academic publications, but are prevalent in internet discussion forums, blogs and “how to” videos. They are designed in much the same way as traditional batteries with copper usually being chosen as the cathode. The anode container is usually made from commercial aluminium cans with the top cut off and the sides sanded to expose the aluminium. For the work presented here, the cathodes were chosen as thin copper plates (or hollow narrow tubes) and an eraser prevented short circuiting between the bottom of the cathode and the base of the container. A basic cement and water mixture was used as the initial electrolyte.

Various mix designs and additives were compared using this battery form and used to examine the natural recharge abilities (or natural charge build-up and storage abilities) when a resistor load was removed for set periods of time.

Cement-based batteries housed in a block

These battery types are similar to the can but both the anode and the cathode are in the form of metal plates (Figure 7). Plastic moulds were used to prevent short circuiting and to allow for a higher volume of sample to be made. These designs were used to compare different additives, anode materials, shapes and sizes.

This type of design is the “best-fit” for cement-based batteries for using with ICCP as they can be incorporated into a cladding panel and fixed onto a structure. For this, particular characteristics are required, namely robustness, long life and a low but consistent current output under resistance load.

4. Results

Layered batteries

Hourly current and voltage measurements were taken from the battery using a 10Ω resistor. A very low current was generated (0.001mA) in the intervening hours but dropped back to 0mA within 10sec. As shown previously by Meng and Chung (2010), the batteries do not work once dried out. After 30 hours all batteries had ceased to output electrical energy.

The air-dried Epsom salt solution did not display any measurable current with only a minor difference upon sealing. Voltage did increase over time as the battery dried as shown in Table 2.

Can batteries

Table 3 presents the results of each mix compared with the basic cement and water combination. As can be seen, there was no noticeable increase in output from the addition of sand with decreases observed when zinc, manganese dioxide were added, as well as increasing the anode ratio. The higher outputs came from increasing the cathode ratio.

An example of the decay in current for the can battery is shown in Figure 8a. As can be seen there is a sudden drop when the open-circuit is lost and the resistor is applied from approximately 19.3 to 4.8mA. Over the next seven days, the current drops below 1mA. Figure 8b shows the natural recharge/storage when the resistor is removed after one month and no current is being drawn out. Regardless of the length of recharge time (one or two hours), the increase in initial current is the same, as is the long-term value.

Block battery results

Voltage and current was measured through a 10Ω resistor and averaged once they became quasi-steady. Figure 9 shows the results from the parametric study. In terms of water to cement ratio (w/c) (Figure 9a), the current steadily increased with water content.

Cathode to anode ratios (Cu:Al) 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4 were created using different cut-plate sizes in the same basic cement paste with no discernible correlation. Distances between electrodes of 5mm, 10mm, 30mm, 60mm and 80mm were compared with no differences in output observed. As per the can batteries, the addition of carbon black (Figure 9b) had a significant impact on the measured outputs with lifespan, current and voltage increases of 33%, 44% and 13% respectively.

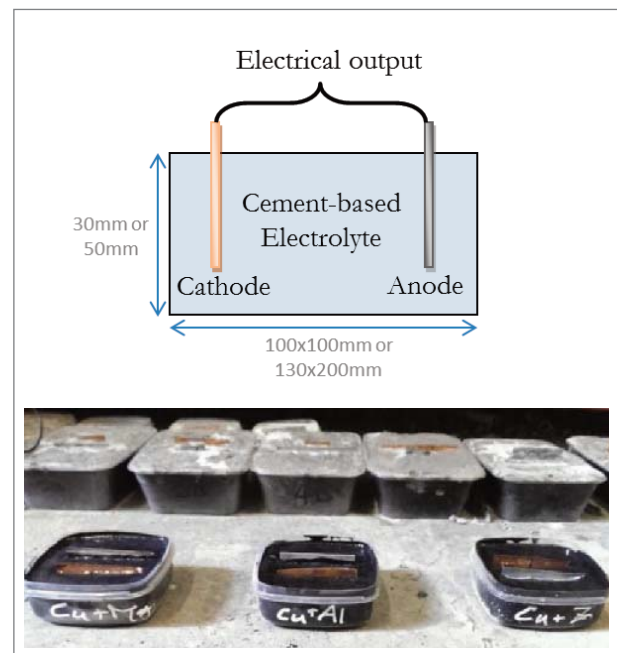


Figure 6: Battery housed in a metal can.

Table 2 – Current, voltage and lifespan results from the layered batteries

Type/Age	0hrs	24hrs	27hrs	30hrs
Epsom solution air dried	V = 0.2V I = 0	V = 0V I = 0	V = 0.995V I = 0	V = 0.489V I = 0
Epsom solution sealed	V = 0.030V, I = 0-0.001mA	V = 0.037V, I = 0-0.001mA	V = 0.23V I = 0-0.001mA	V = 0.51V I = 0-0.001mA
Water air dried	V=0.310, I = 0-0.001mA	V = 0.442 I = 0-0.001mA	V = 0.400V I = 0	V = 0.6V I = 0-0.001mA
Water sealed	V=0.380 I = 0-0.004mA	V = 0.386, I=0.002-0.042mA	V = 0.37 I = 0-0.004mA	V = 0.737V I = 0- 0.001mA

Table 3 – Effect of additives on the power output in the can batteries		
Additive	Current	Voltage
+Sand	=	=
+Carbon black	↑	↑
+Zinc Dust	↓	=
+Manganese dioxide dust	↓	=
Higher anode ratio	↓	↓
Higher cathode ratio	↑	↑

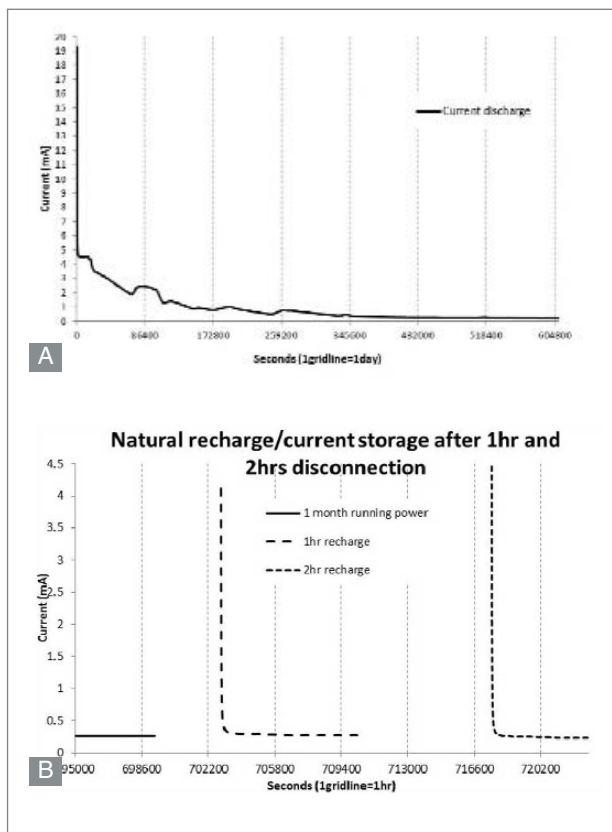


Figure 8: (a) typical current discharge and (b) natural re-charge/storage of a can battery.

The base mix contained only distilled water as the solution. In the other three battery designs, no water was added but different 5-Molar salt solutions were included. These were sodium chloride (NaCl), Alum salt ($\text{AlK08S}_2 \cdot 12\text{H}_2\text{O}$) and Espom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Compared to the base mix, the use of salt solutions decreased the current by 20% (Figure 9c) with Epsom salt having the least loss of 14%.

Voltage also decreased with the addition of the salt solutions. However, the lifespan was greatly increased, by 50% on average. By adding salt to the battery mix in granular form, the current and lifespan increased by 15% and 62.5% respectively, compared to the base mix (Figure 9d).

All battery designs to this point have used copper cathodes and aluminium anodes. Anodes of aluminium, zinc and magnesium were also prepared with the same surface area. The magnesium

anode was in a ribbon shape rather than plate and this may have impacted the results. The zinc anode battery design showed very poor results. However, the magnesium anode battery design provided the highest current and lifespan during testing. Current and lifespan increased by 1000% and 350% respectively compared to the base battery with an aluminium anode.

Initial battery testing, with prioritised current and lifespan, indicates that optimal output could be achieved by designing high w/c ratios, the addition of carbon black, adding salt granules, using magnesium as the anode material and sealing the battery to retain hydration and reaction components and products.

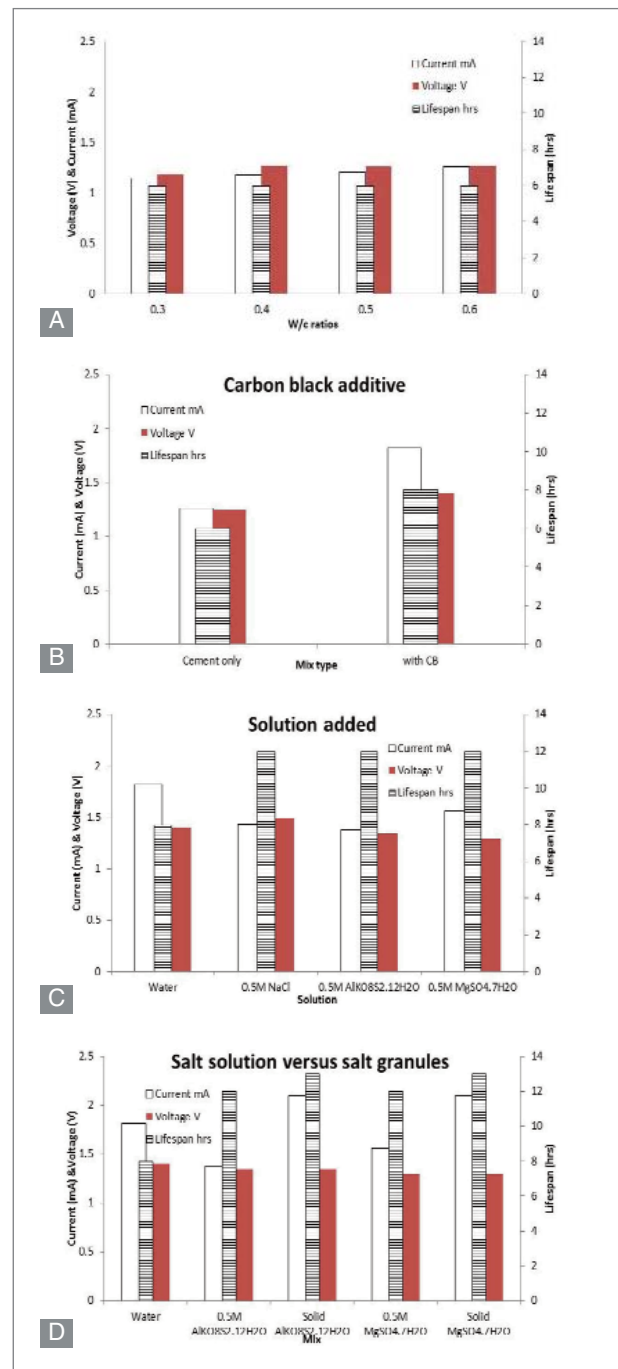


Figure 9: Results of the parametric study to assess the effects of (a) w/c ratio, (b) carbon black additive, (c) salt solution and (d) salt solution and salt granules.

5. Five potential applications of this research for cathodic protection

ICCP limits the corrosion of a metal surface using inert anodes and impressing a current onto the cathode surface using an external direct current (DC) source. For steel reinforcement the recommended (Polder *et al*, 2009) design current density is 20mA/m^2 , which refers to the circumferential surface of the bars. While the currents seen here are low, previous work has shown that lower values for protective current can be successfully used in ICCP to prevent embedded steel corroding (Polder *et al*, 2009; Glass *et al*, 2001; Glass and Chadrick, 1994; Glass and Buenfeld, 1995; Koleva *et al*, 2006; McArthur *et al*, 1993).

There have been limited but reliable examples of where intermittent current supply has provided adequate cathodic protection to structures (Glass *et al*, 2001; Glass and Chadrick, 1994; Glass and Buenfeld, 1995; Koleva *et al*, 2006; McArthur *et al*, 1993; Christodoulou *et al*, 2010; Kessler *et al*, 1998). The ability of cement-based batteries to recharge when the load is removed has been shown here. Stand-alone cement batteries could power the process using a switching mechanism between individual units allowing them to discharge and recharge multiple times.

6. Conclusions

Can-shaped batteries have shown to have the longest lifespan. However, these batteries have a very low output range and need further development. Connecting them in parallel or series to increase output is ongoing.

Carbon black proved to increase output, particularly current and increase longevity due to its ability to increase the connectivity between conductive materials. However, due to its fineness, it makes the batteries considerably brittle so a water reducer is essential.

Although salt solution increased longevity, adding the same salts in solid granule form was even more beneficial and increased current output. When salts are dissolved in water they break up and move through the liquid.

Copper was consistently used as the cathode material in all tests as it is highly noble and easily available. Comparing aluminium, zinc and magnesium anodes, it was found that magnesium produced a substantial improvement in all areas, particularly current and longevity. Open circuit potential values of -1.344V for untreated magnesium, -0.786V for zinc and -0.524V compared to copper (Bullis, 2014) indicates that the highest outputs should occur for magnesium followed by zinc and aluminium.

Layered cement batteries cease to work once dry and this paper presents some first steps in sealing layered-style batteries. Further research into different sealing techniques could help maintain moisture and therefore increase the longevity of batteries.

The possibility of connecting cement-based batteries in parallel has not yet been explored in the research but could be a way of increasing the current output and longevity from the batteries.

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