https://doi.org/10.18321/ectj1438

Designing Water-Repellent Concrete Composites Using Cheap Organic Materials

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Article info

Received:
24 May 2022

Received in revised form:
15 July 2022

Accepted:
10 September 2022

Abstract

In this paper, it was successfully established a novel and cheap water-proofing technique for protecting concrete from further damage caused by water leakage. This technique originated from the proper design and rational formulation of the materials including hydrophobic sand, silicon oil, tyre crumb rubber, and recycled motor oil. From this research, it can be seen that only one concrete showed hydrophobicity and all obtained concrete demonstrated significantly and in some cases extremely low water permeability relative to control concrete. To the best of current knowledge, this is the first paper, which studied the surface and water sorption properties of concrete modified by the addition of hydrophobic sand obtained by patented technology. The goniometer investigated the surface properties of the modified concrete. The results obtained including density, contact angle, change of weight, and maximum load capacity under high electro-hydraulic pressure were compared and discussed.

1. Introduction

Concrete is a widely-used construction material in the world because of its advantages such as cheapness, strength and easy-process ability. However, due to the low resistance to water its durability may deteriorate gradually [1]. The presence of a large number of pores and flaws provides primary access to the inner structure of the concrete due to the capillary action; hydroxyl groups formed after the cement hydration serves as additional factors to facilitate hydrophilic behavior on the concrete surface [2]. All these issues may accelerate the deterioration of cement by inducing corrosion of steel in reinforced concrete [3, 4], chemical attacks [5], carbonation [6], and many other types of degradation.

Generally, the protection methods of the concrete are classified as the following two:

(i) pre-treatment of the cement – premixing the cement major composition with functional components in the cement mortar;

(ii) post-treatment of the cement – modifying concrete's surface after the hardening [1].

Surface post-treatment is based on blocking pores/flaws and creates a covering layer as a water-repellent coating. The disadvantage of the post-treatment is frost damage, abrasion, and short-term durability [7, 8]; Specifically, abrasion resistance is the main challenge for such a technique.

In order to prolong the durability of the concrete, it's important to avoid the concrete inner structure from direct contact with water and moisture. The foremost strategy is to create hydrophobic concrete to prevent the concrete from water penetration, which can be realized by applying rationally-designed materials in combination with corresponding techniques. Hydrophobicity also may reduce or even block the attachment of microbes [9, 10] that produce sulfuric acid, etc. The residues may also chemically attack the concrete surface to induce corrosion [5].

The hydrophobic concrete, prepared by pre-treatment techniques, contains hydrophobic components within its entire structure and its hydrophobic property doesn't suffer from outer surface cracking, abrasion, and pore formation [11, 12].

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The most seen materials used to create hydrophobic property for the concrete are PDMS (polydimethylsiloxane) [13], PFDTS (perfluorodecyltriethoxysilane) [14], PMHS (polymethylhydrosiloxane) [15], stearic acid [16], nano silica [17] and even copper mesh with stearic acid [18]. Also, in recent decades, a certain used engine oil acting as an imparting hydrophobic component in cement mortar has been attracting attention [19–22].

The use of the above material may serve as a free chemical substitute for other hydrophobic agents, which results in a positive environmental effect, which is avoiding releasing it into the environment. Finding an appropriate way to utilize recycled engine oil may stop its illegal disposal. Another intriguing waste product from the automotive industry is crumb rubber, which is obtained after tires are usually sheared until small particles. They are mostly applied on the surface of roads and sport yards. That can be used as a filler to obtain light concrete [23].

In this paper, we plan to develop hydrophobic concrete to prevent water penetration and improve the lifetime of the concrete. In order to reach the goal, hydrophobic concrete can be developed based on the two hypothesis (1) waste oil components induce the hydrophobic property for concrete, (2) crumb rubber lead to roughness and hydrophobicity since the micro-nano level roughness is an essential requirement for hydrophobicity. Thus, we prepared different cylindrical concrete through mixing the preselected materials such as silicon oil, waste engine oil, crumb rubber, and hydrophobic sand [24] in the mortar containing the major component, cement. Previously, our university patented technology of hydrophobic sand obtaining [24], and that is why in this series of experiments an additional line of samples was added hydrophobic sand as a hydrophobic agent. Also, we used silicon oil as a cheap mixture of siloxanes, hence, siloxane PDMS showed promising results [13].

Water absorption behaviors of these concretes were further tested in parallel with their contact angle (CA) measurement analysis. The surface property of concrete was evaluated by a goniometer. Their mechanical property was also tested in correlation with the above measurements [25, 26].

2. Experimental part

2.1. Materials

Construction cement (type M500) was used to form concrete in a cylinder form. Washed and dried river sand was sieved using a test sieve (Retsch™, micromesh sizes ≤800 μm). Hydrophobic sand was synthesized from the sieved river sand according to the patented technology [24]. Silicon oil was purchased from Sigma Aldrich®. Fresh motor oil (Hyundai® XTeer) was purchased in the market with the following characteristics: synthetic, 5W-30, Gasoline G700. The same used motor oil was taken out from the 3.8-liters engine of the vehicle (Kia Mohave) after around 7 000 km of running. Tap water was used for the whole experiment. Sheared crumb rubber recycled from vehicle tyres (≈0.6–1 mm particle size) was kindly provided by LLP "Rubber technical wastes" (Rubber recycling plant, Astana, Kazakhstan).

2.2. Methods

The general experiment design is presented in a graphical abstract (Fig. 1).

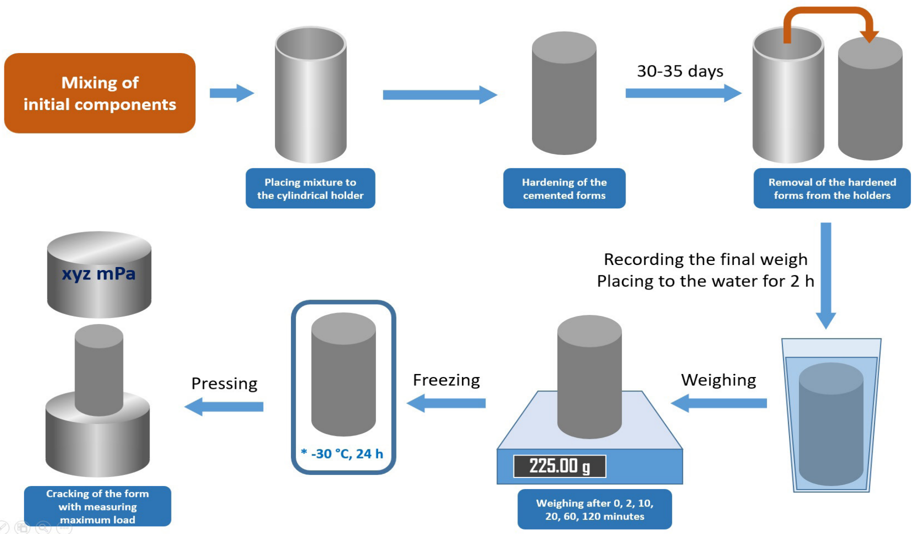


Fig. 1. Scheme of preparation and formation of concrete cylinders.

Table 1
Mass ratios of initial components for samples preparation

Sample name	Cement	Sand	Water	Silicon oil	Motor oil	Rubber
Control	1	1	0.4	-	-	-
Hydrophobic sand	1	1[a]	0.4	-	-	-
Silicon oil	1	1	0.4	0.125	-	-
Rubber + Silicon oil	1	1	0.4	0.125	-	0.4
Fresh Motor oil	1	1	0.4	-	0.127[b]	-
Used Motor oil	1	1	0.4	-	0.127[b]	-
Used Motor oil	1	1	0.4	-	0.127[c]	-

a – was used hydrophobic sand instead of regular sand; b – for 5.0% concentration of oil; c – for 2.5% concentration of oil.

2.2.1. Characterization of motor oils

In order to show the significant chemical difference, the absorbance of motor oils – fresh and used – was measured in UV-visible region 200–800 nm using Evolution 300 spectrometer (ThermoScientific®). For this purpose, 50 µl of each oil was diluted in 1 ml of hexane and placed into a plastic disposable cuvette. For the baseline, pure hexane in the cuvette was used.

The size of formed particles inside of these oils was defined by Dynamic Light Scattering (DLS) technique using ZetaSizer® NanoZS (Malvern®).

2.2.2. Formation of cylinder forms

A plastic polypropylene cylindrical cup with an inner diameter 47 mm and a height 100 mm was used to produce cylindrical concrete. Cement, water, sand and hydrophobic agents were mixed at the calculated mass ratios (see Table 1). To briefly summarize, the mass ratio of sand/cement/water (S/C/W) was fixed at the ratio of 1:1:0.4 in all samples. In the sample of "Hydrophobic sand", the hydrophobic sand was used as a hydrophobic agent. For other samples, different amounts of oils mentioned in Table 1 were added. Then, after the mixing of the initial components, each mixture was placed in plastic cylindrical cups for a period 30–35 days in order to achieve the best hardening. Finally, the net weights of all concrete forms were measured.

2.2.3. Water sorption by cylindrical concretes

After the hardening period, the plastic cups were broken, then the concrete forms were extracted to use for water absorption tests. Before the experiments, the net weights were measured. Then, tap water was poured onto each concrete placed into the thin dish or 220 ml of tap water was enough to cover the cylinder with dimension 47×100 mm completely. In order to see the trend of water absorption, each cylinder was removed after 2, 10, 20, 60 min, wiped thoroughly, and then the weight was measured. After 2 h of water immersion, each cylindrical concrete was put out. Finally, the weight was recorded again (Table 2).

2.2.4. Additional stress of cylindrical forms in the fridge

All cylindrical concrete forms after the water experiments (section 2.2.2) were wiped well with paper wipes and then placed in the fridge at -30 °C for 24 h.

2.2.5. Measurement of maximum load capacity

The measurement of the maximum load capacities was held by a universal testing machine (LR-WAW-1000D Microcomputer control electrohydraulic servo universal testing machine). The rate of the press machine was set to 1 mm/min for all samples.

3. Results and discussion

The research goal of this works is to improve the life time of the concrete and construct water-repellent cheap concretes based on our hypothesis below: (1) cheap hydrocarbon oils leads to hydrophobic property; (2) hydrophobic particles such as crumb rubber and hydrophobic sand creates the roughness which is an essential requirement for the super-hydrophobic property. To obtain water-

Table 2
Characteristics of prepared samples

Sample	ρ, g/ml	CA(3), °	Weight growth(2), %	Maximum load, mPa	Bars number
Control	1.64 ± 0.10	0	+5.1	26.95(2,3) 25.26	1 2
Silicon oil	1.575 ± 0.05	63.03	+0.3	11.61(2,3) 14.96	3 4
Hydrophobic sand	1.56 ± 0.05	98.62	+0.3	17.61(2,3) 19.04	5 6
Rubber + Silicon oil	1.35 ± 0.10	79.46	+0.68	2.88(2,3) 3.31	7 8
Fresh motor oil 5%	1.525 ± 0.05	72.42	+2.14	7.14(2,3) 8.64	9 10
Used motor oil 5%	1.495 ± 0.05	73.22	+0.63	2.72(2,3) 4.1	11 12
Used motor oil 2.5%	1.57 ± 0.10	73.18	+2.7	12.14(2,3) 12.8	13 14

(1) CA – contact angle; (2) – after 2 h of water action; (3) – after 24 h of frost action.

repellent concrete, the following materials such as hydrophobic sand, silicon oil, fresh and used motor oils, and sheared crumb rubber as hydrophobic agents were added to the major components of concrete (water, sand, cement).

Interestingly, the physical properties of fresh and used motor oil differ not only by colour and absorbance, but by the size of formed nanoparticles as well (Fig. 2).

Fresh motor oil absorbs the light in an invisible UV region 240–340 nm forming a doublet peak with approximately equal shoulders, almost fully transparent and has a yellow colour. Small aggregates of fresh oil molecules 5 nm in size were detected by DLS.

Used motor oil oppositely has a wider highly intensive absorption spectrum and different shoulders ratio in a doublet peak making it fully non-transparent with black colour. More than that, the average size of oil aggregates for the used oil increased 6 times and consists of around 30 nm sized particles.

The water absorption degree of the concrete forms was analyzed in terms of time, and compared with their initial strength. The degree of "water-repellency" was determined by a contact angle measurement tool, goniometer, and weight growth of the cylindrical concrete after a long stay in the water. All cylindrical forms after the addition of hydrophobic agents demonstrated a significant increase in contact angle from a totally water-absorbing surface to 63° and higher. Although only one cylindrical concrete possessed a large contact angle (above 90°), all samples still displayed a significant decrease in the water absorption degree owing to having a water-repellency.

Therefore, a shearing process in the vehicle engine destructed significantly oily chains and changed its physico-chemical properties.

The selection of the hydrophobic agent for inducing hydrophobic and water-repellent properties in the concrete is an initial important step, which should lead to a high contact angle. For this aim, silicon oil was used to test since its major components are hydrocarbons, in addition, its price is cheaper than the PDMS. The second hydrophobic component is a used motor oil from the vehicle's engine since it is another form of the hydrocarbon mixture. In comparison, fresh motor oil was selected.

Based on the second hypothesis, rubber crumb, the product of tire recycling, along with silicon oil was added to construct cylindrical light water-repellent concrete, in addition, it will reduce the weight of the concrete as a lightening material. At the same time, hydrophobic sand (obtained by technology belonging to Nazarbayev University and patented in 2016) covered with a thin layer of a number of hydrophobic components including siloxanes, was selected to make a hydrophobic concrete. The contact angle of this sand varies in the range of 150–160° (Fig. S1).

A control sample consisting of cement, water and regular sand after the hardening was tested to check water absorbing capability. The control

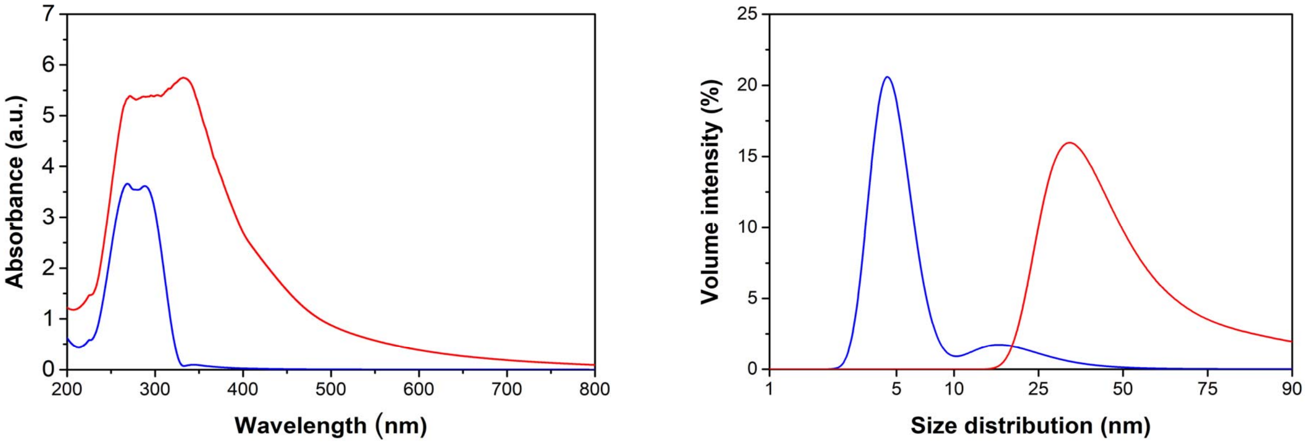


Fig. 2. UV-Vis absorption spectrum and size distribution of — Fresh motor oil, — Used motor oil (dilution in hexane 80 times).

sample demonstrates super-hydrophilic properties. The contact angle is close to 0° in any circumstances. To build the hydrophobic concrete, the amount of the sand in the control experiment (sand/cement/water (S/C/W)) as shown in Table 1, was replaced by hydrophobic sand and the selected components.

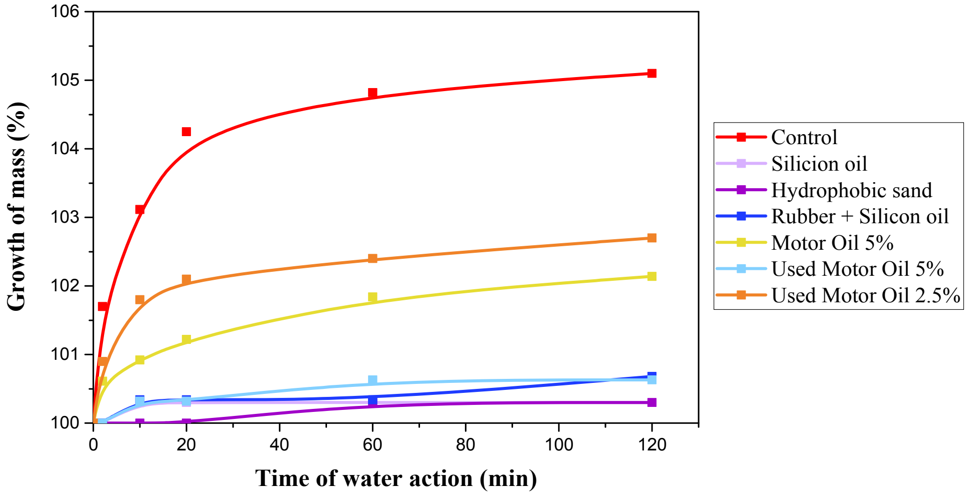
The contact angle of the concrete created by hydrophobic sands was increased to 98° (Table 2). In all other cases, surfaces were transformed from super-hydrophilic to hydrophilic. Their contact angles varied between 60–80° and did not exhibit hydrophobic behavior. Therefore, addition of silicon oil to the S/C/W mixture increased the surface contact angle until 63° only. It was a minimal value of growth among all samples. Interestingly, an analogous sample but with addition of rubber crumb showed an increase of contact angle until 79°. It can be explained that the rubber crumb consists of small soft particles with irregular shapes less than 1 mm in size, and may impart additional roughness to the surface. Moreover, the theory of hydrophobicity states that the roughness is one of the influencing factors. In addition, the density of this sample became significantly less to form light concrete compared with the control sample, or its density changed from 1.64 g/ml to 1.35 g/ml (Table 2). This result indicates that addition of rubber crumb is a clever way to construct light concrete, which may be an object of interest in construction.

Rest of the samples modified with fresh and used motor oils also showed the reduction in density until around 1.5 g/ml and stable contact angle around 72–73° for all three concretes. This confirms the previous trend that any addition of hydrophobic material serves as a water-repellent agent already at mixing step and prevent water penetration for the cylindrical concrete forms.

Even after addition of hydrophobic agents, contact angles did not grow significantly and only in one case exceeded 90° (in order to be considered as hydrophobic). This does not mean that this concrete will absorb the water. Long stay of prepared samples in the vessel containing water during a 2 h experiment was held to see the change of concretes' weights after the probable water absorption.

The control sample showed +5.1% of weight increase, which is expected since the cement tries to fulfill all non-hydrated bonds of its oxides with the water molecules to form hydrogen bonds. Compared to the control sample, all other samples demonstrated low water absorption capability according to the weight change.

Two samples – fresh motor oil (5%) and used motor oil (2.5%) – absorbed less than the control, but higher than other samples. These 2 samples showed weight growth +2.14 and +2.7% respectively (Table 2). The other samples demonstrated extremely poor water absorption and their weight growth did not exceed +0.7% (Fig. 3a and 3b). In comparison of two analogous samples consisting of mass of 5% of oils, fresh and used, there is a huge difference in weight change (+2.14% and +0.63% respectively), or the concrete made of fresh motor oil had more than three times that of the concrete based on the used motor oil. It can be explained that the latter was exposed to the mechanical shearing in the vehicle engine, most of the chains were broken up and some amount of solid residue particles were present in its content.



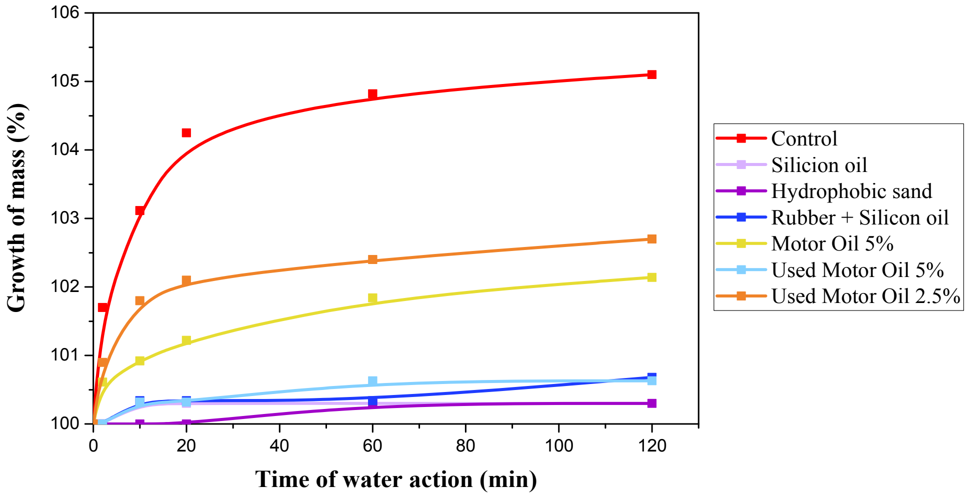


Fig. 3. Water absorption by cylindrical forms within the time (increase of weight in %% by mass): a) – all samples; b) – enlarged region for samples with hydrophobic sand, used motor oil 5%, silicon oil and mixture of crumb rubber and silicon oil.

Solid residue particles participate in surface structuring and forming the mentioned above roughness. Nevertheless, half the amount of the used motor oil (2.5% by mass) in the sample was followed by increased water absorption and the weight growth became almost the same as for the sample with fresh oil.

The mechanical property of the above cylindrical concrete forms was evaluated by fracture test or cracking under high pressure and the highest load capacity. The control samples consisting of a regular sand, cement and water demonstrated the highest load capacities for both, for the sample exposed to a long water action and a freeze, and for the sample not exposed to mentioned actions (Fig. 4). It is noticeable that the bar #1, corresponding to the sample exposed to water action and freeze, is a little bit higher than the bar #2. In all other cases, samples exposed to water action and freeze showed the opposite result.

4. Conclusion

A simple and cost-effective technique for the improvement of concrete's lifetime was developed by using cheap materials resources. The mechanical and water absorption capability of the concrete relative to conventional concrete has been significantly changed. Especially when including the addition of the waste material, tire rubber crumb, indicated the potential development of lightweight concrete in the future. Also, to our best knowledge, for the first time, this work investigated the water sorption by change of weight of obtained concrete with the inclusion of hydrophobic sand, obtained by our technology [24].

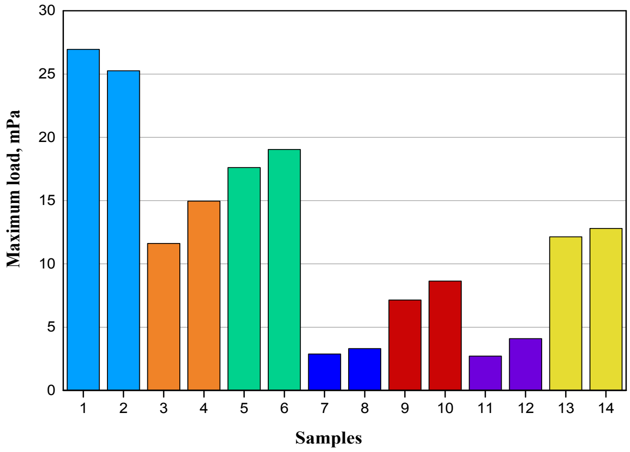


Fig. 4. Bars graph of maximum loads of the prepared cylinders: 1, 2 – control; 3, 4 – silicon oil; 5, 6 – hydrophobic sand; 7, 8 – crumb rubber + silicon oil; 9, 10 – fresh motor oil (5%); 11, 12 – used motor oil (5%); 13, 14 – used motor oil (2.5%). Uneven numbers of bars – samples were exposed to the water action and fridge, and then cracked; even numbers of bars – samples were cracked without additional stress exposure.

This is a simple materials processing and manufacturing technique without containing expensive steps such as heat supply, vibration, etching, chemical vapor deposition, etc. On the other hand, the desired result of appropriate water repellency was achieved for major samples. That all indicates the low price of the final product.

Nevertheless, modified concrete showed lower stability against compressive stress, it might be used in the waterproofing of roofs, walls and other sites without high pressure or load due to its low water impermeability.

Acknowledgements

This work was supported by a grant from the Ministry of Education and Science of the Republic of Kazakhstan (grant number AP08052848).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.18321/ectj1438.

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