A new kind of concrete for fire protection

Prof. Dr. rer. nat. Bernd Spangenberg, Simon Girsch B.Sc., Prof. Dipl. Ing. Dietmar Kohler

Das Institut NaSiO (Institut für Nachhaltige Silikatforschung in Offenburg, https://inasio.hs-offenburg.de/) arbeitet seit Jahren an klimafreundlichen Alternativen zu Dämmstoffen und anorganischen Bindern, wie auch dem sinnvollen Einsatz von Bauschutt in der Bauindustrie. Ziel der Forschung ist die Realisierung der enormen CO_2-Einsparpotenziale, die im Bausektor weltweit möglich sind. Ein Stoppen der Klimaerhitzung wird nur gelingen, wenn in der Bauindustrie diese klimafreundlichen Alternativen zum Einsatz kommen, denn nur so lassen sich die vor uns liegenden enormen CO_2-Einsparungen realisieren, die zur Einhaltung des Pariser Abkommens nötig sind.

The NaSiO Institute (Institute for Sustainable Silicate Research in Offenburg, https://inasio.hs-offenburg.de/) has been working for years on climate-friendly alternatives to insulation materials and inorganic binders, as well as the reasonable use of construction waste in the building industry. The aim of research is to realize the enormous CO_2 saving potential of the construction sector worldwide. A stopping of climate heating will only succeed if these climate-friendly alternatives are used in the construction industry. This is the only way to realize the enormous CO_2 savings that will be needed in future to comply with the Paris Agreement.

Problem definition

On December 14, 2020, the Badische Zeitung reported the fire of a Citroen Berlingo that caught fire while driving [1]. The fire risk of cars is still underestimated, and certainly will get worse in the future with increased use of electric cars. It happens again and again that because of a fire in an underground car park the whole building above has to be demolished because its stability is no longer guaranteed. The cause of such structural damage lies in the low stability of conventional concrete at high temperatures of over 650 °C [2].

In recent years concrete has also been in the headlines for two other issues. The production of concrete consumes a lot of river sand, which will no longer be available in future. The phrase „like the sand of the sea", familiar from the Bible, applies no longer, because the inexhaustible sand deposits on or in the sea have long been a thing of the past. There is still plenty of sand worldwide, but only in sand deserts, which account for about 20 % of the world's desert areas. In the industrialized countries, the raw material quartz sand is slowly becoming scarce. River sand is needed in the construction sector because desert sand is largely unsuitable there for use. Its round grains, abraded by the wind, do not adhere to each other and cannot be used for concrete [3].

The biggest problem of modern concrete is only tentatively addressed in public: Approximately 0.80 tons of CO_2 are released per ton of cement produced. Due to the huge quantities of cement consumed worldwide (approx. four billion tons of cement in 2016), the cement industry is responsible for 5 to 8 % of anthropogenic carbon dioxide emissions. Most people are not aware of this problem with concrete, and it becomes clear when compared to the emissions from air travel that are so often in the headlines. While total air traffic resulted in CO_2 emissions of about 700 million tons per year in 2018, emissions from the cement industry were well over two billion tons of CO_2[4].

Against this background, there is an urgent need to search for new binders that have lower CO_2 emissions. Such new binders for example must be able to bind desert sand and they must be sufficiently stable at high temperatures. This is the reason, the NaSiO Institute (Institute for Sustainable Silicate Research in Offenburg) was founded. Here, research is still being carried out on the chemical conversion of water glass in combination with aluminates to form temperature-stable binders. Water glasses are colorless aqueous solutions of sodium and potassium silicate. The acronym NaSiO stands for the chemical formula of sodium water glass.

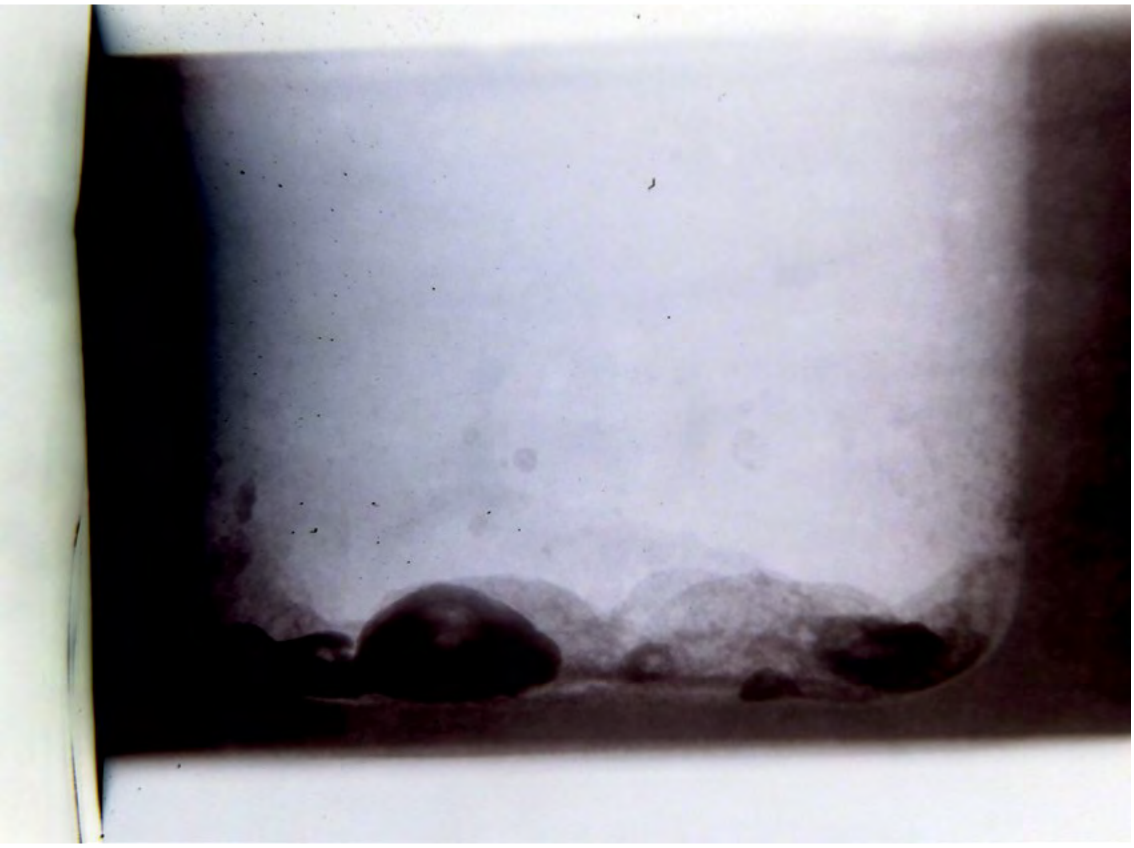

Fig. 1:
X-ray image of desert sand mold with iron lumps on the ground

The formula is $Na_2Si_sO_{2s+1}$, where *s* describes the modulus value, the molar ratio of silicon dioxide (SiO_2) to sodium oxide (Na_2O). Water glasses have modulus values of 1.5 to 5, depending on their silicon dioxide content. Water glasses react with aluminates to form polymeric Si-O-Al structures that have concrete-like properties. Water glass is produced from sand and soda or from sodium and potassium hydroxide. The energy required for production today comes from petroleum, but direct use of solar energy is also conceivable. A future water glass industry will probably be located near salt lakes in desert areas and, due to the availability of soda ash, (desert) sand and plenty of sunlight, will operate according to the so-called s^3 process.

Results and discussion

Testing of the new inorganic binder against heat

Concrete is stable up to temperatures of approx. 200 °C. At higher temperatures, however, its strength decreases rapidly. Above 500 °C, concrete is destroyed as the heated top layer of a few centimeters flakes off, because the water, bound in the concrete, evaporates. The rapid heating of concrete surfaces can lead to veritable explosions, with larger pieces of concrete flying off the surface [5]. Charging stations for electric vehicles should therefore be protected from fires and especially from melted battery components by a fire-resistant coating [6]. The increasing number of electric car registrations impressively shows that this problem must be solved in the next few years.

To test the heat resistance of the new binder, a hollow mold (in the form of a beaker) was made from 800 g of Chinese desert sand, 172 g of water glass and 100 g of aluminate. The Si/Al ratio of the binder is 0.72. For its production, 70 % less CO_2 is released than for a concrete production of comparable strength, if the electricity used for production comes from renewable sources. The desert sand which was used, came from China and had an average grain size of about 130 μm with a very narrow grain size distribution. Thus, when referring to desert sand it is better to speak of sand dust. The mold cast produced with this sand had a bottom thickness of only about 7 mm. A thermite mixture consisting of 8.5 g aluminum powder and 25 g iron oxide was ignited in this mold. An X-ray image taken afterwards showed no damage to the mold bottom by the molten iron, which is visible as cherry-sized oval deposits in the X-ray image (figure 1). Where the iron was in contact with the bottom of the mold, only a few small stress cracks appeared.

The image in figure 2 (top) shows the repetition of the experiment, performed outdoors with four times the amount of thermite. (The shower of sparks observed compensated for the corona-related fireworks ban on New Year's Eve 2021.) After the chemical reaction, the white-hot liquid iron covered the entire bottom of the vessel. Within a few minutes, the molten iron cooled on the surface, showing a yellow-orange color (figure 2, bottom). The melting point of iron is 1538 °C. The iron produced in the reaction (in an amount of 88 g) was heated far above this. According to the Encyclopaedia Britannica, iron reaches a temperature of up to 2400 °C in a thermite reaction and forms a slightly mobile light yellow to whitish liquid [7]. It can be assumed that during the experiment the bottom of the vessel for a short time was exposed to a temperature of about 2400 °C.

Fig. 2:
Thermite reaction (left top) to 88 g of liquid iron (left bottom)

Testing results of the new inorganic binder against heat

After the iron had cooled, the mold was cut open in the middle and the mold surface was examined more closely at the iron contact points. The pre-damaged mold bottom showed a number of new small stress cracks, but withstood the load as no iron was leaking (figure 3). The newly developed stress fractures did not crack even when the mold was cut. At the points of contact with the molten iron, the new binder discolored slightly and flaked off in some places (figure 3). This can be explained by the enormous temperature differences during the reaction in the mold. The new binder did not lose stability during the thermite test, because a layer about 3 mm in thickness remained at the bottom of the mold when it was cut, although the thermally unstressed binder broke here. All this speaks rather against damage and in favor of a solidification of the mold due to heat exposure.

Figure 3 and figure 4 show very nicely the amazingly large number of air bubbles in the molten iron. In the enlargement of image 3 (please see figure 4), not only the porous structure of the iron at the contact point can be seen, but also the fine binder structure of the mold. The sand grains are difficult to see. The temperature-dependent discoloration of the new binder can be seen very clearly. Clearly visible is the stress cracking that occurs at the interface between heated and unheated material, but not within the heated area. Partial melting of the mold surface (figure 4, center of image, top) can also be seen, resulting in an intimate bond between the iron and the sand of the mold. The tests carried out show that the novel binder can withstand temperatures of about 2400 °C in the short term and can be used as a vessel for molten iron.

Fig. 3:
Image of the mold cut open in the middle (external dimensions: 10 cm x 10 cm x 10 cm)

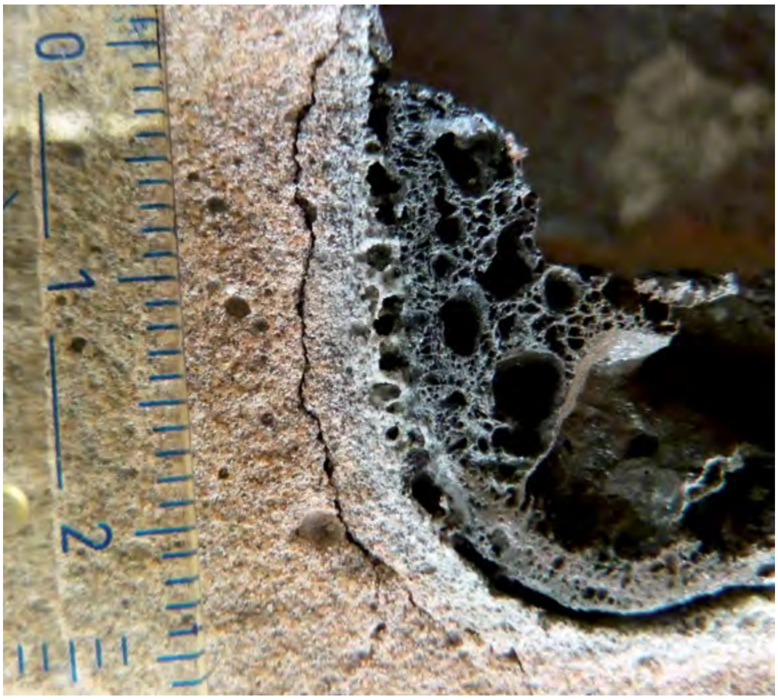

Fig. 4:
Enlargement of the contact area between the mold and the molten iron

Summary and outlook

The novel binder in its mixture with sand can be handled and mixed like conventional concrete. It cures at room temperature within a few hours and can be demolded after 24 hours. Its compressive strength can be freely adjusted in a range between 10 and 160 N/mm² via the additive content. At a compressive strength of 40 N/mm², its CO_2 footprint is about 70 % lower than the CO_2 emission of a comparable high-performance concrete. As shown, the novel binder is stable at high temperatures and can thus be used for fire protection. For underground garages, an interior plaster a few millimeters thick would be conceivable as a protective layer for the structural concrete, possibly combined with a layer of heat-insulating material. Of course, underground parking garages could also be cast entirely from the new binder.

This is particularly recommended for E-mobile charging stations, as these are a critical component of a new E-mobile infrastructure. At an elevated temperature, and especially during rapid charging, a lithium-ion battery can thermally runaway and catch fire. It then releases all of its stored energy within seconds and can easily set other E-mobiles on fire. Thermal runaway of lithium-ion batteries can result in temperatures exceeding 700 °C, depending on the state of charge of the battery [8]. Future charging stations for E-mobiles in underground garages should be cast from the new binder in the form of a trough to prevent liquid metal from spreading the fire. In this way, the new charging structure for E-mobiles to be built could also extend to underground garages or built-over areas without the need to demolish the entire superstructure in the event of a fire.

In summary, the novel binder enables the production of a concrete from desert sand and water glass that can withstand contact with molten iron. Its production releases significantly less CO_2 than conventional concrete. The novel binder is marketed under the name VITAN®.

Referenzen/References:
[1] https://www.badische-zeitung.de/hilfsbereitschaft-nach-autobrand-war-gross--198874578.html (retrieved 28.12.2020)
[2] Fire and Concrete Structures, (2008), https://www.cement.org/docs/default-source/th-buildings-structures-pdfs/fire-concrete-struc-sei-08.pdf
[3] Sand, rarer than one thinks, UNEP; https://wedocs.unep.org/handle/20.500.11822/8665 (retrieved 28.12.2020)
[4] Horst-Michael Ludwig, Neuartige Bindemittel – Die Zeit nach dem Portlandzement, in: Betone der Zukunft (2018), 49-57, https://www.baufachinformation.de/mobil/buch/betone-der-zukunft-herausforderungen-und-chancen-14/250455 (retrieved 28.12.2020)
[5] https://www.youtube.com/watch?v=NxJPX0lsslQ (retrieved 28.12.2020)
[6] Prof. Dr. rer. nat. Werner Schröder, personal notification, ViCircle (14.02. – 15.02.2020), Stuttgart
[7] Thermit (chemical compound) in: Encyclopaedia Britannica, https://www.britannica.com/science/Thermit (retrieved 28.12.2020)
[8] X. Liu, S. I. Stoliarov, M. Denlinger, A. Masias, K. Snyder, Comprehensive calorimetry of the thermally-induced failure of a lithium ion battery, Journal of Power Sources 280 (2015) 516 – 525, http://dx.doi.org/10.1016/j.jpowsour.2015.01.125 (retrieved 28.12.2020)

AUTOREN

Prof. Dr. rer. nat. Bernd Spangenberg
Head of the Institute NaSiO
Fields of teaching: chemistry, chemical analytics, waste and recycling technology, bionics
spangenberg@hs-offenburg.de

Simon Girsch B.Sc.
Bachelor's degree in process engineering
Member of the Sustainable Silicates research group at the NaSiO Institute
simon.girsch@hs-offenburg.de

Prof. Dipl. Ing. Dietmar Kohler
Deputy Head of the Institute NaSiO, Dean of the Faculty of Mechanical & Process Engineering, areas of teaching: materials engineering/ testing and welding technology
dietmar. kohler@hs-offenburg.de