



Use of MID-MIX[®] treated sewage sludge in cement mortars and concrete

Journal:	<i>European Journal of Environmental and Civil Engineering</i>
Manuscript ID	TECE-2017-0433.R1
Manuscript Type:	Original Papers
Date Submitted by the Author:	15-Mar-2018
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Keywords:	sewage sludge, thermal treatment, cement, mortars, concrete

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Developing beneficial applications for sewage sludge is a key challenge in many countries, given the amount of sludge generated and the disposal or recycling options currently available. Sewage sludge from the wastewater treatment plant at Koprivnica in Croatia has been treated using MID-MIX[®] technology that involves the addition of Ca(OH)₂ and CaO to dewatered sludge. This produces a low-density non-hazardous white-grey powder. The treated sewage sludge has been heated to 800, 900 and 1000°C to form MID-MIX[®] treated sewage sludge ash with reduced organic content. MID-MIX[®] treated sewage sludge and ash have been used to replace 10 and 20% of cement in mortar and concrete samples. The addition of MID-MIX[®] treated sewage sludge causes a significant increase in void content which reduces the mechanical properties and durability of mortar and concrete samples. However, replacement of cement by MID-MIX[®] ash did not significantly affect the strength, water penetration or gas permeability compared to control samples. Leaching tests on MID-MIX[®] powder, MID-MIX[®] ash and mortar samples produced low levels of heavy metal release. The research shows that thermally processed MID-MIX[®] treated sewage sludge produces an ash product that has potential to be beneficially used in cementitious materials for selected applications.

Keywords: sewage sludge; thermal treatment; cement; mortar; concrete

Introduction

Sewage sludge management is critically important to prevent environmental pollution as the pollutants entering a wastewater treatment plant (WWTP) are concentrated into the sludge. Landfill of sewage sludge is not an acceptable disposal option under EU regulations. Incineration reduces sewage sludge weight by approximately 70% and volume by 90% (Lynn, Dhir, Ghataora, and West, 2015) and produces a sewage sludge ash. At the EU level about 22% of generated sewage sludge is incinerated, but the high costs associated with this technology make it uneconomic for many countries (Lynn, Dhir, Ghataora, and West, 2015). In Croatia, approximately 35% of the total population

(1,512,985 inhabitants) is connected to the 110 active municipal WWTP that provide variable levels of wastewater treatment (Vouk, Serdar, Nakic, and Anic-Vucinic, 2016). It is expected that, by the end of 2020, there will be WWTP capacity for 4,300,000 population equivalents. Sewage sludge disposal in Croatia varies significantly at different utility companies. Sludge is disposed of in landfills for solid waste, significant quantities are disposed of within the perimeter of WWTPs, a very small proportion of sludge is used in agriculture and it is not clear how a significant fraction of sludge is currently managed (Vouk, Serdar, Nakic, and Anic-Vucinic, 2016). Sludge management in Croatia is a major problem that has not been solved and solutions are not defined by regulations, instructions or guidelines. As construction of WWTP in Croatia increases driven by the EU, sludge disposal will become an increasing problem for utility companies responsible for wastewater treatment.

MID-MIX[®] is a relatively low-cost waste treatment technology used since the 1980s for processing various industrial wastes (Yunirisk Int., 2014). It is a physical-chemical oxido-reduction process involving the reaction of wastes with additives based on calcium CaO and Ca(OH)₂ and it produces an inert granular product and steam. The technology is recognized by the EU as the best available technology for treating selected wastes from the oil and petro-chemical industries, pharmaceutical wastes, food processing wastes and wastewater treatment sludge.

A schematic diagram of the MID-MIX[®] process used to treat sewage sludge is given in Figure 1. After dewatering to 25% dry matter, the sludge enters the pre-storage dehydrated sludge tank. From this tank, the dewatered sludge is transferred by conveyor belt to the MID-MIX[®] pre-reactor where it is thoroughly mixed and homogenised with Ca(OH)₂. CaO is then added in the MID-MIX[®] reactor and the resulting exothermic reaction releases ~1.18 MJ/kg CaO. This is sufficient to break down aromatic and

organic compounds and cause the evaporation of internal cell and internal capillary water present in the sludge. The share of added $\text{Ca}(\text{OH})_2$ (in the form of pure hydroxide and mostly in the form of recirculated solidificate) is about 20-30% and the proportion of added CaO is about 20%, both relative to the mass of the sludge dry matter. The reaction mix then passes to the terminator where the product cools. This is followed by the final tank where optimal conditions exist for the physicochemical process of solidification. The previously initiated dissociation of molecules continues through the process of vacuum-gas encapsulation and the formation of complex stable organic structures of the sludge biomass in the presence of quicklime to produce carbon dioxide stabilised as CaCO_3 (Valderrama, Granados, and Cortina, 2013), where different ligands from the waste material are permanently bound. The temperature of the resulting 'solidified' material is quite high at the reactor exit, so the material is cooled by passing through an additional processing unit which extends the reaction time. After cooling to $\sim 40^\circ\text{C}$ the treated product is loaded into jumbo bags for temporary storage.

Treating sewage sludge with the MID-MIX[®] process produces a white-grey inert granular powder, referred to as MID-MIX[®] sewage sludge (MSS). This can be disposed of at a non-hazardous waste landfill in accordance with EU regulations. However, it would be beneficial from an environmental and circular economy perspective if the MID-MIX[®] treated sludge could be used as a secondary raw material (Brkljac, Sevic, Beker, Kesic, and Milisavljevic, 2012; Yunirisk Int., 2014). The overall aim of ongoing research is to develop optimum solutions for sludge disposal in Croatia. The aim of the specific research reported in this paper was to evaluate the potential for using MID-MIX[®] sewage sludge (MSS) and MID-MIX[®] sewage sludge ash (MSSA) as a part substitute for the cement binder used in the production of mortars and concrete.

Materials and methods

Materials

Sewage sludge was obtained from the WWTP at Koprivnica, Croatia. This uses sequential batch reactors and tertiary treatment. The sewage sludge generated by the plant was then treated using MID-MIX[®] technology. The product of the MID-MIX[®] treatment (MID-MIX[®] treated sludge, MSS), is a low-density white-grey powder that does not require additional drying as it is around 90% dry matter (Brkljac, Sevic, Beker, Kesic, and Milisavljevic, 2012). To enhance the reactivity for incorporation into cementitious materials, the MSS powder was thermally treated at temperatures of 800 for 3 hours, and 900 and 1000°C for 2.5 hours, to produce MID-MIX[®] sewage sludge ash (MSSA). These times were previously determined as required for the complete decomposition of the sludge (complete combustion of organic matter) at each temperature since the further combustion did not change the mass of the remaining ash at the given temperature. The thermal treatment removes residual organic matter that would adversely influence cement hydration reactions and produces various mineral transformations which are compatible with those witnessed in cement which is beneficial from a reactivity perspective.

Preparation of mortar and concrete samples containing MSS and MSSA used Portland cement containing slag and limestone (CEM II/B-M (S-V) 42.5N), dolomite sand (0/4mm) and ordinary tap water, with a water to binder ratio of 0.50. Mortar batches were prepared in a 5-litre mixing bowl, with 2534 g of binder (cement and substitution with MSS/MSSA). Concrete samples were prepared in a 75-litre concrete mixer, with 22.5 kg of binder (cement and substitution MSS/MSSA).

The mortar and concrete samples were prepared with different amounts of MSS and MSSA partially substituting for cement (0, 10 and 20%) as shown in Table 1.

Mortar mixes containing MSSA required addition of a superplasticizer (MasterGlenium SKY 629, BASF Chemicals) to achieve equivalent workability to the control mix. As an example, compositions of mixtures with 20% SSA obtained at 900°C are given in Table 2 (mortar) and Table 3 (concrete).

Methods

The density of the MSS and MSSA samples produced at different temperatures was measured following ASTM C-188 – 17 using a Le Chatelier flask. The chemical composition of samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using the method described in HRN EN ISO 11885:2010. The particle size distribution was determined using air jet sieving (A058-05N) in accordance with HRN EN 933-10:2009 for the classification of fillers.

X-ray diffraction (XRD) was performed on MSS and MSSA samples to evaluate the mineralogical composition of powders and the effect of thermal treatment. Samples were scanned between 5 and 80°, using a step size of 0.02° and a time per step of 0.6 s (Shimadzu XRD-6000, with CuK α radiation). Qualitative analysis of diffraction patterns was performed using the ICDD diffraction data base and software (X'PertHighScore Plus). The morphology of MSS and MSSA particles was examined using scanning electron microscopy (SEM, Tescan Vega 3 instrument). Heavy metal content was determined by digesting samples in Aqua Regia (HCl and HNO₃ in ratio 3:1) and metal concentrations were determined using flame (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS). Other parameters were determined by water elution.

The temperature of mortar and concrete samples was monitored following HRN U.M1.032 1981 using a pinhole digital thermometer. The workability of fresh mortar samples was measured using standard cone samples on a flow table. The flow table

spread (FTS) was calculated from the average value of the maximum and minimum diameters of the spread cone in accordance with HRN EN 1015-3:2000/A2:2008. The workability of fresh concrete samples was determined using a standard truncated cone for slump testing in accordance with HRN EN 12350-2. The air content was determined using the pressure method following HRN EN 1015-7:2000 for fresh mortars and HRN EN 12350-7 for concrete.

Mortar specimens for strength testing were prepared as 4 x 4 x 16 cm prisms. Nine specimens were made from each mix using steel moulds, with three tested at each curing age (1, 7 and 28 days). Specimens for gas permeability testing were 100 mm Ø, 160 mm high cylinders. Concrete specimens for compressive strength testing and water penetration depth were 15 cm cubes and flexural strength and shrinkage testing used 10 x 10 x 40 cm prisms. All the specimens were de-moulded after 24 hours and cured in a humidity chamber (relative humidity >95%, temperature 20±2°C). Mechanical tests were performed following HRN EN 1015-11:2000/A1:2008 on mortars and according to HRN EN 12390-3 and HRN EN 12390-5 on concrete. Mortar samples were tested in bending and then the two resulting parts were tested in compression.

Gas permeability tests were performed on three specimens of each mortar mix, using the RILEM Cembureau method. Test specimens were oven dried at 105°C for 24 hours. The pre-conditioning of samples did not follow the procedure described in the RILEM recommendations. All specimens were pre-conditioned using the same procedure so that the gas permeability coefficient obtained could be used to compare different mixes. Water penetration depth on concrete samples was determined on three specimens of each mix in accordance with HRN EN 12390-8.

Total shrinkage of concrete was tested following HRN U.M1.029. Each test result was the average of tests on three 10 x 10 x 40 cm prisms. Specimens were de-

moulded 24 hours after casting and two sets of measuring pins were glued onto the two opposite sides of the specimens and these were then stored in a chamber at a controlled temperature of 20°C and relative humidity of 60%. To determine the shrinkage of each specimen, the mean value of two shrinkage measurements on opposite sides of the prisms was determined. Measurements were performed every 7 days for 90 days.

Leaching tests used the compliance leaching test for granular waste materials and sludge (EN 12457-2). The samples tested were MSS and MSSA obtained at 900°C, and samples of crushed cement mortars cured for 28 days containing 20% of MSS or MSSA obtained at 900°C. These mortars were the same as those used for other tests.

Results

Physical and chemical characteristics of MSS and MSSA

The chemical composition of MSS and MSSA samples produced at different combustion temperatures is given in Table 4 and the concentration in heavy metals is given in Table 5. Previous research has shown that sewage sludge ash can contain significant amount of phosphate, usually between 10 and 20% by mass, and this can delay cement hydration reactions and reduce initial concrete strengths (Lynn, Dhir, Ghataora, and West, 2015). In the case of tested MSS and MSSA, the amounts of phosphate were significantly lower.

As the combustion temperature increased the mass reduction of sludge increased by about 2% per 100°C. The average mass reduction at 800°C was ~26%, at 900°C it was ~28% and it was ~30% at 1000°C. MSS has a dry mass content of >96% and for MSSA the dry mass is even higher. Both materials can be classified as low in organic and moisture content.

Thermal treatment removes a significant amount of organic matter from MSS and the percentage of CaO is increased as shown in Table 4. The density of MSS was 2.10 g/cm^3 . The density of MSSA samples produced at different incineration temperatures increased from 2.78 g/cm^3 at 800°C to 2.90 g/cm^3 at 900°C and 2.95 g/cm^3 at 1000°C .

The concentrations of heavy metals in MSS and MSSA shown in Table 5 are low. The concentration of heavy metals in sewage sludge is influenced by the type of industrial activity in the area serviced by the WWTP. Since Koprivnica is in a region of Croatia with limited industrial activity, obtained low concentrations of heavy metals are expected.

The results of air jet sieving of MSSA and MSS show no significant differences in particle size distribution that can be related to the combustion temperature. The particles ranged between 5 and $500 \mu\text{m}$ (Figure 2), with most particles between 20 and $63 \mu\text{m}$. However, it has to be highlighted that the air jet sieving method has certain limitations, mainly in evaluation with precision distribution of particles smaller than $10 \mu\text{m}$. For more precise evaluation of particle size distribution of smaller particles methods such as laser diffraction would be more appropriate. Using more precise method for evaluating size distribution of smaller particles would potentially reveal more significant difference in fineness between ashes combusted at different temperatures.

XRD data for MSS indicates large crystallites and the absence of amorphous phases. The main crystalline phases are calcite (CaCO_3) and portlandite (Ca(OH)_2), which is consistent with the calcium-rich chemical composition, while secondary crystalline phases are anhydrite (CaSO_4), dolomite ($\text{CaMg(CO}_3)_2$) and illite. XRD of thermally treated MSSA samples are typical for complex samples with a large amount of crystalline phases and substantial amorphous phase. For the sample generated at

800°C the main crystalline phases are portlandite, lime (CaO) and calcite, with some quartz (SiO₂) and anhydrite. The samples processed at higher temperatures show very similar crystalline phases, although there is a reduction in calcite at 900°C and it is almost absent from the sample obtained at 1000°C. The decrease in calcite is because it decomposes at temperatures between 600 and 800°C (Lothenbach, Durdzinski, and De Weerd, 2016). Thermal degradation of calcite produces lime and this is the major crystalline phase in the MSSA sample treated at 1000°C. After thermal treatment and prior to XRD analysis, carbonation may form calcite in MSSA samples processed at 900 and 1000°C.

The SEM images in Figure 3 show that the particles have different size and shape characteristics. The particle size distribution of MSS observed by SEM is narrow, with the most of the particles ranging from 0.2 - 1 µm. However, particles are quite agglomerated and form a porous isomorphic mass. It is for that reason that when using air jet sieving method much higher values of particle sizes were obtained, since it is the size of these agglomerates that is measured and not the size of individual particles. The MSSA samples had similar morphology with poly-disperse grains and irregularly shaped particles. The degree of agglomeration is slightly greater than for MSS and the porosity in the agglomerates is less clear. The differences are primarily reflected in a more uniform particle form and size distribution centred ~0.5 µm. With increasing combustion temperature, the grains become more defined with sharper edges. Areas with different chemical composition are not observed and the distribution of different phases is homogeneous.

Effect on properties of fresh mortars and concrete

No segregation or bleeding was observed in mixes containing MSS or MSSA. All mixes containing MSSA showed compliance with reference values for density of fresh mortar and concrete and minimum differences between mixes were observed. Mixes containing MSS showed a slight decrease in density of ~10%. Densities in fresh condition were between 2.25-2.55 g/cm³.

When MSS was used in mortar and concrete mixes, there was no marked increase in the temperature of fresh mixes. With the addition of the MSSA a significant increase in the temperature of the fresh mortar and concrete was observed, up to 8°C increase compared to control mixes. There was an increase in water demand for mortars and concrete containing MSSA, while when MSS was used no significant decrease in workability was observed. Mixes containing higher amounts of MSSA showed significantly lower flow table spread (FTS) and slump values and these mixes required higher additions of superplasticizer, up to 0.8% by mass of total binder.

The air content of fresh mortar/concrete increased with increasing content of MSSA. The increase is not linear and the air content was found to increase an average of about 25% with the addition of 10% of MSSA in mortars and nearly 35% in concrete, whereas 20% MSSA resulted in a ~45% increase in mortar and ~80% increase in concrete samples. There were no significant differences in air content for mixes containing MSSA obtained at different combustion temperatures. When MSS was used as partial cement replacement, the air content of fresh mortar/concrete increased even more. With the addition of 10% of MSS, the air content of fresh mortar was approximately doubled, and with the addition of 20% of MSS it more than quadrupled. In concrete mixes the increase in air content was even greater. For samples containing 20% of MSS the air content was 7.5%, a five times increase when compared to the

control mix. Tables 6 and 7 show all the fresh properties of mortar and concrete samples tested.

Effect on properties of hardened mortars and concrete

Mechanical properties

Mechanical property data of mortars indicates that increasing replacement of cement with MSS and MSSA decreases the compressive and flexural strengths. This is particularly evident for MSS, while using MSSA processed at higher temperatures significantly reduced the decline in strengths. The strength loss was much more evident in mortars than concrete (as shown in Figures 4 and 5). Most of the concrete mixes incorporating MSSA showed strength values equivalent to the reference mixture, and some mixes containing MSSA had higher values than control mixes.

Considering all the mortar samples tested (Figure 6), the highest 28-days compressive and flexural strength were obtained for the control mix, while all the mixes containing MSS or MSSA developed significantly lower strengths.

The properties of the concrete samples containing 10% MSSA obtained at 900 and 1000°C (Figure 7) are worth highlighting. Concrete samples containing 10% MSSA formed at 900°C had greater flexural and compressive strengths than control samples. The highest compressive strength was developed using 10% of MSSA fired at 1000°C which had 10% greater compressive strength than the control mix (Figure 7). The highest 28-days flexural strength was obtained for the sample with 10% MSSA obtained at 900°C. This had 6% greater flexural strength than the control mix. The lowest strength values were recorded for samples with incorporated MSS for all tested ages of concrete.

Durability properties

Increasing the amount of MSS in mortars increased the permeability coefficient (Figure 8). Similar results were recorded when MSSA produced at 800°C was used, but with a slightly smaller increase in permeability coefficient. When MSSA obtained at higher combustion temperatures was used, especially MSSA produced at 1000°C, a positive effect on the gas permeability of mortars was observed, as the permeability coefficient was less than the control mortar.

The class of mortars containing MSSA produced at 800 and 900°C in terms of gas permeability remained the same as the reference mortar, but when MSSA produced at 1000°C was used the class of mortar improved from “low resistance” to “medium resistance”. Mortars containing MSS were all classified as very low resistance mortars. Because the samples were fully oven dry before testing and the temperature of drying was 105°C, it is likely that the coefficients of gas permeability are greater than the “real” gas permeability of samples pre-conditioned using the procedure recommended by RILEM (Geiker, Grube, Luping, Nilsson, and Andrade, 1995).

When MSS was used in concrete the water penetration depth increased by ~40% with the addition of 10% MSS and ~50% with the addition of 20% MSS (as shown in Figure 9). This is expected given the porosity and the air content recorded in these mixes in the fresh state. This increase in water penetration depth is much less apparent using MSSA. Lower combustion temperatures seem to reduce the detrimental effect on the water penetration depth of concrete. When 10% of MSSA fired at 800°C was used in concrete the water penetration depth was slightly reduced compared to the control mix.

Shrinkage data obtained from drying concrete samples is shown in Figure 10. The use of MSS has a major adverse effect on the volume deformations of hardened

concrete. Total shrinkage of concrete samples with 20% MSS after 90 days was increased by ~55% compared to the reference concrete. However, the effect of thermally treated MSSA on the volumetric deformations of concrete was positive. Concretes incorporating MSSA obtained at 800°C showed deformation similar to the reference concrete, while concrete samples containing MSSA obtained at higher temperatures showed noticeably reduced total shrinkage. The lowest shrinkage was observed for the samples with 20% MSSA obtained at 1000°C; after 90 days. This had 25% less shrinkage than the control concrete.

Long-term behaviour – environmental impact

The EN 12457 leaching test is used to determine the type of landfill a particular waste can be sent to (i.e. hazardous, non-hazardous or inert). Leaching of heavy metals such as Mo, Se and Sb can make sewage sludge unsuitable for disposal in inert waste landfill (Chen and Lin, 2009). Leaching tests produced leachate solutions with pH ~ 12 for mortar samples and ~12.4 for samples of MSS and MSSA. The results for MSS and MSSA are compared to the relevant waste acceptance criteria in the EU Landfill Directive in Figure 11. The samples meet the criteria for inert waste for all analyzed elements except Mo. Leaching of Mo from the MSS and MSSA was above the limits for inert waste (Figure 11) and therefore these materials would be classified as non-hazardous waste. This is in agreement with previous research on sewage sludge ash (SSA) which showed that Mo and Se were the critical elements (Chen, Blanc, Gautier, Mehu, and Gourdon, 2013).

Figure 11 also shows Mo leaching data for mortar samples containing 20% MSS and 20% MSSA fired at 900°C. Mo leaching from crushed mortars incorporating MSS or MSSA was below the limit for categorization as inert waste. Therefore MSS/MSSA-mortars, when crushed at end-of-life, could potentially be sent to inert waste landfill or

recycled as construction and demolition waste and used as aggregates in road bases and concrete.

Discussion

MID-MIX[®] technology produces a MSS product predominantly composed of CaO, mostly in the form of calcite and portlandite. MSS and the thermally treated secondary product MSSA generated using sludge from the WWTP at Koprivnica contain relatively low concentrations of heavy metals and organic matter and therefore the potential to use them as mineral admixture in cement mortars and concrete has been investigated.

When MSS was added as 10 or 20% replacement of cement the resulting concrete had reduced compressive and flexural strengths and increased permeability and water penetration depth, compared to the reference concrete. This reduction in performance suggests that direct application of the MID-MIX[®] sludge product is not possible. The chemical composition of MSS is not ideal for use in cementitious materials and the high residual organic matter is likely to inhibit cement hydration reactions and entrap air during mixing. The morphological structure of MSS particles is also not ideal as these tend to consist of porous agglomerates, as seen in the SEM images in Figure 3a). The extremely high air content and porosity found in mortars and concrete samples prepared with MSS is a consequence of the high organic matter and agglomerated particles that do not break down during mixing. The high air content in mixes with MSS produced a weaker cementitious matrix, as observed by the decrease in compressive and flexural strength compared to reference mortar and concrete. The porous matrix allows penetration of gas and water, especially under pressure, which is evident through increased gas permeability and water penetration depth for mixes with MSS compared to the reference concrete. A reduction in mechanical properties has previously been reported for sewage sludge ash (SSA) addition and in most cases the

compressive and flexural strength decrease linearly with increasing percentage of cement substitution by SSA (Chen and Lin, 2009; Garcés et al., 2008; Pan et al., 2013; Tay, 1986). This negative effect of SSA was explained by the excessive water content required in mixtures to maintain workability due to the roughness and irregularity of SSA particles and the accessible inner porosity (Monzó, Payá, Borrachero, and Girbes, 2003). The same reasons can explain the negative effect of MSS on the mechanical and durability properties of concrete. Negative influence of MSS on concrete properties is additionally caused by the residual organic matter in MSS.

MSSA has been produced by heat treating MSS at temperatures between 800 and 1000 °C to remove the residual organic component. This significantly reduces the organic matter and produces improved particles with less pronounced porosity as seen in Figures 3 b)-d). For these reasons, the impact of MSSA addition on concrete air content is less pronounced and is in the same range as the reference concrete. The addition of MSSA decreases the workability of concrete; for the same workability more water is needed. The increased water demand is due to the irregular morphology and small particle size, producing high specific surface area. A similar influence on workability and water demand was reported for conventional types of sewage sludge ash (Monzó, Payá, Borrachero, and Girbes, 2003; Cyr, Coutand, and Clastres, 2007; Vouk, Serdar, Nakic, and Anic-Vucinic, 2016). High water demand can have a negative influence on concrete properties and was compensated for by the addition of superplasticizer so that MSSA mixes had the same workability as reference mortar and concrete mixes. In comparison to MSS, samples prepared with thermally treated MSSA have lower air content in fresh mixes and higher compressive and flexural strength. Selected mixes had improved mechanical properties compared to reference concrete, particularly mixes with 10% of MSSA_900°C and MSSA_1000°C. The higher

1
2
3 reactivity of MSSA compared to MSS is observed from the initial concrete temperature
4 rise. With MSSA the temperature of fresh concrete increased, indicating rapid hydration
5 reactions. This is attributed to the high content of CaO compared to MSS, as indicated
6 from XRD. Since cement with slag was used in the mix, it is possible that the presence
7 of slag in the cement and presence of CaO in the ash led to pozzolanic reaction leading
8 to the formation of C-S-H, which has for a consequence, greater compressive strength
9 development in mixes with MSSA. The improved properties of mixes with MSSA are
10 reflected in the permeability data of these mixes. The reduced permeability of MSSA-
11 containing mortars and concrete is explained with the higher reactivity of MSSA
12 compared to MSS, leading to finer pore structure. The “filler effect”, where MSSA
13 particles fill the gaps between larger aggregate grains in concrete may also occur.
14 MSSA also has a positive influence on the drying shrinkage of concrete. The
15 significantly higher drying shrinkage of mixes with MSS can be explained by the
16 excessive drying of unreacted MSS particles when concrete samples are placed in a dry
17 environment, while particles of MSSA react with water and cement and do not cause
18 excessive drying, resulting in lower drying shrinkage.

39 Conclusions

40
41 Sewage sludge from the WWTP at Koprivnica in Croatia was treated with MID-MIX®
42 technology to produce a powdery MSS product containing high lime content. The
43 application of MSS in mortars and concrete has been investigated but produces high
44 entrapped air, influencing both the mechanical and durability properties. This effect is
45 attributed to the high residual organic matter and the porous agglomerated MSS
46 particles. Thermally treating MSS forms MSSA, and both the mechanical and durability
47 properties of concrete and mortar samples are enhanced using MSSA relative to MSS
48 and are similar to those of control samples. Leaching of Mo is an issue from MSSA but

this is significantly reduced when it is used in mortars and concrete. It is concluded that MSSA obtained by thermally processing MID-MIX[®] treated sewage sludge has potential to be beneficially used in cement mortars and concrete for use in selected applications.

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Table 1. Mortar and concrete mixtures included in experimental research

Mix label	MSS/MSSA (as a substitute for cement)	Thermal treatment temperature	Superplasticizer (relative to the mass. of binder)
	[%]	[°C]	[%]
Mortar mixes	Control	0	-
	MSS_10%	10	-
	MSS_20%	20	-
	MSSA_800°C_10%	10	800°C
	MSSA_800°C_20%	20	800°C
	MSSA_900°C_10%	10	900°C
	MSSA_900°C_20%	20	900°C
	MSSA_1000°C_10%	10	1000°C
	MSSA_1000°C_20%	20	1000°C
Concrete mixes	Control	0	-
	MSS_10%	10	-
	MSS_20%	20	-
	MSSA_800°C_10%	10	800°C
	MSSA_800°C_20%	20	800°C
	MSSA_900°C_10%	10	900°C
	MSSA_900°C_20%	20	900°C
	MSSA_1000°C_10%	10	1000°C
	MSSA_1000°C_20%	20	1000°C

Table 2. Composition of mortar mixture MSSA_900°C_20%

Component	Mass [kg]	Density [kg/dm ³]	Volume [dm ³]
Cement	405.44	2.95	137.44
MSSA (20%)	101.36	2.90	34.95
Water	253.40	1.00	253.40
w/b = 0.50			
Air (2.5%)			25.00
Superplasticizer (0.70% mass of the binder)	3.55	1.10	3.23
Agregate 0-4 mm	1501.46	2.75	545.99
Total	2265.21	2.27	1000.00

Table 3. Composition of concrete mixture MSSA_900°C_20%

Component	Mass [kg]	Density [kg/dm ³]	Volume [dm ³]
Cement	240.00	2.95	81.44
MSSA (20%)	60.00	2.90	20.69
Water	150.00	1.00	150.00
w/b = 0.50			
Air (2.5%)			25.00
Superplasticizer (0.80% mass of the binder)	2.40	1.10	2.18
0-4 mm (49%)	971.13	2.75	353.14
Agregate 4-8 mm (20%)	396.38	2.75	144.14
8-16 mm (31%)	614.39	2.75	223.41
Total	2434.30	2.43	1000.00

Table 4. Mean values of weight percentages (wt. %) of major oxides in MSS and MSSA

Oxide (wt. %)	MSS	MSSA 800°C	MSSA 900°C	MSSA 1000°C
CaO	64.83	92.82	93.13	93.83
SiO ₂	1.26	0.49	0.86	0.41
Al ₂ O ₃	1.27	0.89	0.88	1.19
Fe ₂ O ₃	0.33	0.39	0.39	0.40
MgO	0.45	0.71	0.55	0.77
P ₂ O ₅	0.93	0.80	0.45	0.83
TiO ₂	0.03	0.04	0.03	0.05
Na ₂ O	0.05	0.04	0.10	0.03
K ₂ O	0.10	0.12	0.55	0.13
SO ₃	0.73	1.40	0.87	1.15
remaining	0.52	2.37	2.19	1.20

Table 5. The concentrations (mg/kg) in heavy metals in MSS and MSSA

Parameter	MSS	MSSA 800°C	MSSA 900°C
Cu	20.0	33.1	28.8
Zn	59.6	815	240
Cr	1.8	2.7	0.8
Co	6.0	18.4	8.2
Ni	-	172	94.6
Cd	0.1	1.2	0.3
Pb	-	7.0	3.3
Mo	2.1	16.0	9.8
SO ₄ ²⁻	6.7	3	2
Total dissolved solids (mg/L)	46000	3340	3810
Dissolved organic carbon (mg/L)	360	19.8	16.8

Table 6. Properties of fresh mortar samples

Mix	FTS [mm]	Air content [%]	Density [g/cm ³]	T [°C]
Reference	160.0	1.5	2.33	21.5
MSS_10%	161.5	3.1	2.28	21.8
MSS_20%	157.5	6.5	2.21	22.2
MSSA_800°C_10%	165.0	1.8	2.31	27.8
MSSA_800°C_20%	162.5	2.1	2.26	31.0
MSSA_900°C_10%	165.0	1.7	2.32	27.5
MSSA_900°C_20%	162.5	2.2	2.27	37.8
MSSA_1000°C_10%	150.0	2.1	2.32	27.1
MSSA_1000°C_20%	155.0	2.2	2.30	37.4

Table 7. Properties of fresh concrete samples

Mix	Slump [cm]	Air content [%]	Density [g/cm ³]	T [°C]
Reference	11	1.5	2.52	25.3
MSS_10%	9	5.8	2.38	24.8
MSS_20%	10	7.5	2.34	25.8
MSSA_800°C_10%	10	2.2	2.50	27.8
MSSA_800°C_20%	9	3.0	2.50	35.7
MSSA_900°C_10%	9	2.1	2.53	31.4
MSSA_900°C_20%	8	3.1	2.53	37.7
MSSA_1000°C_10%	10	1.8	2.54	27.8
MSSA_1000°C_20%	8	1.9	2.46	34.6

Figure 1. Schematic diagram of the MID-MIX[®] process used to treat dehydrated sludge

Figure 2. Particle size distribution of MSS and MSSA obtained at different incineration temperatures

Figure 3. SEM micrographs and XRD data with crystalline composition of the a) MSS, b) MSSA_800°C, c) MSSA_900°C, and d) MSSA_1000°C

Figure 4. Effect of curing time on the compressive strength of mortars with incorporated MSS/MSSA as a partial substitute for cement

Figure 5. Effect of curing time on the compressive strength of concrete with incorporated MSS/MSSA as a partial substitute for cement

Figure 6. Compressive and flexural strengths of mortar for age of 28-days depending on the proportion and the type of added MSS/MSSA

Figure 7. Compressive and flexural strengths of concrete for age of 28-days depending on the proportion and the type of added MSS/MSSA

Figure 8. Gas permeability coefficient of mortars depending on the proportion and the type of added MSS/MSSA

Figure 9. Water penetration depth of concrete depending on the proportion and the type of added MSS/MSSA

Figure 10. Shrinkage of concrete depending on the proportion and the type of added MSS/MSSA

Figure 11. Leaching concentrations of Mo and their comparison with relevant WAC limits for European landfills

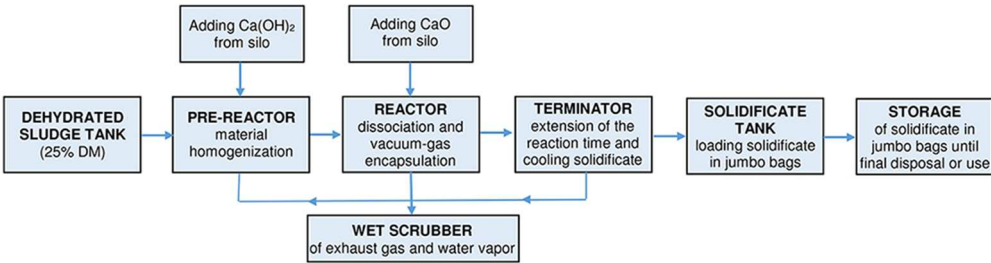


Figure 1. Schematic diagram of the MID-MIX® process used to treat dehydrated sludge
96x29mm (300 x 300 DPI)

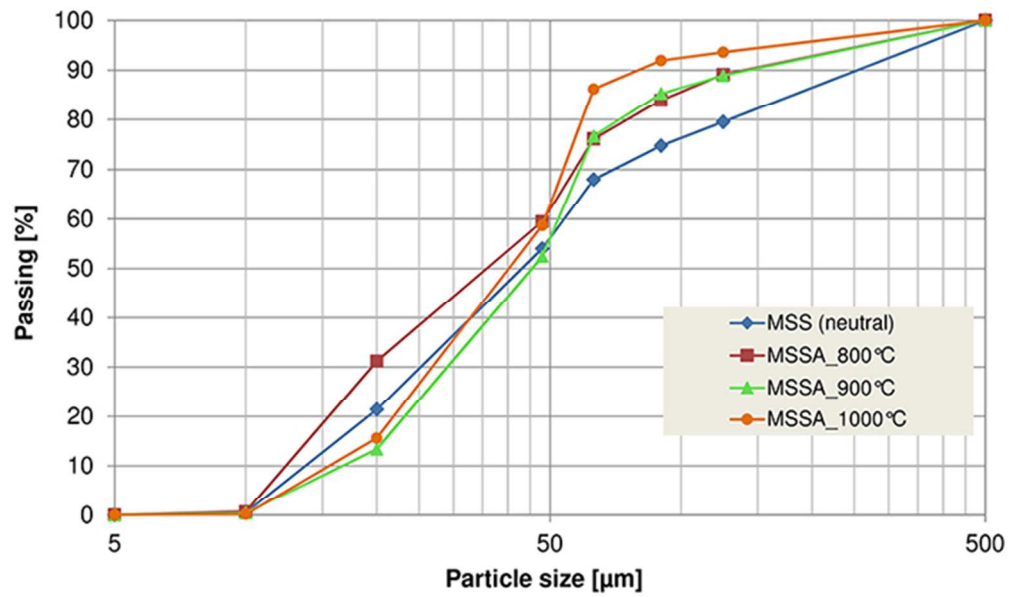


Figure 2. Particle size distribution of MSS and MSSA obtained at different incineration temperatures

59x34mm (300 x 300 DPI)

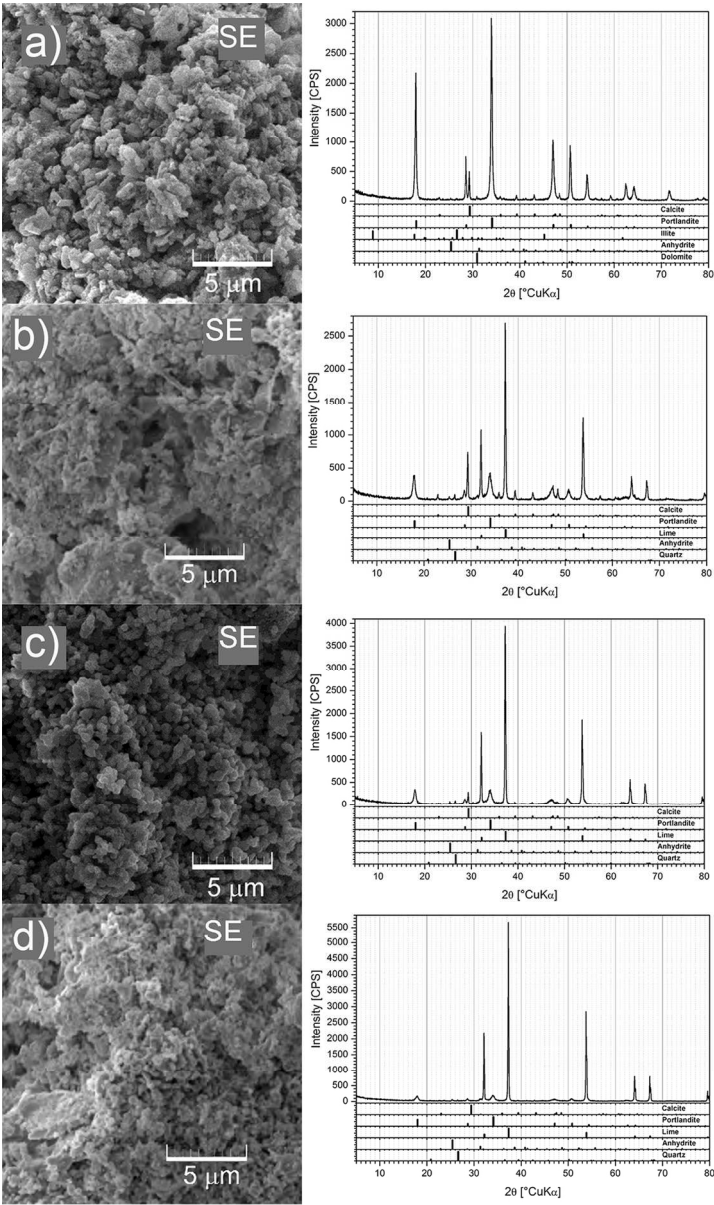


Figure 3. SEM micrographs and XRD data with crystalline composition of the a) MSS, b) MSSA_800°C, c) MSSA_900°C, and d) MSSA_1000°C

109x183mm (300 x 300 DPI)

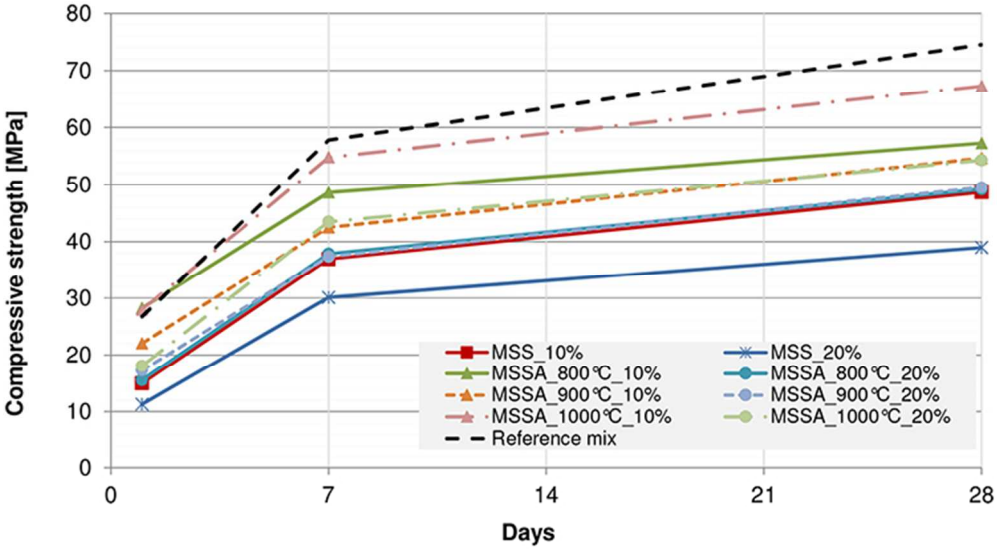


Figure 4. Effect of curing time on the compressive strength of mortars with incorporated MSS/MSSA as a partial substitute for cement

63x34mm (300 x 300 DPI)

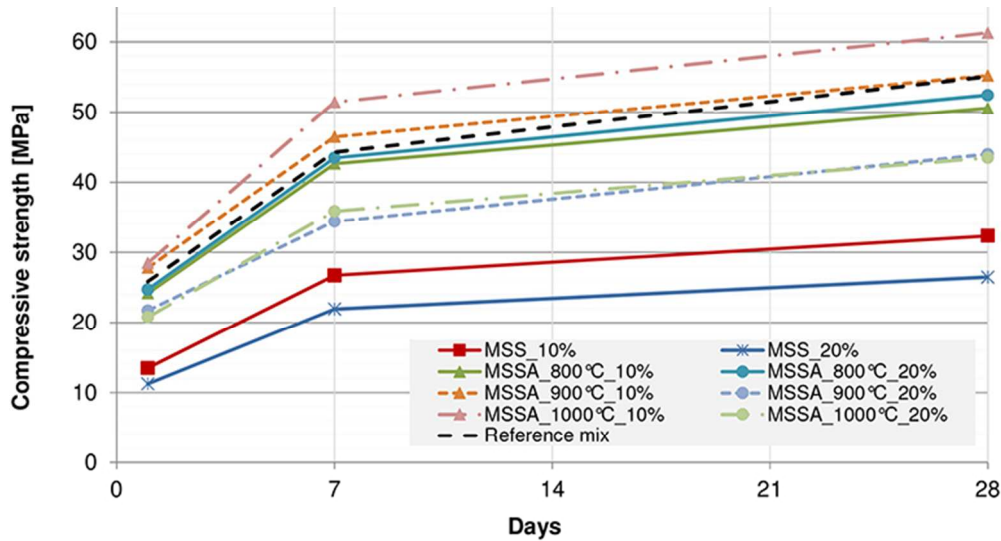


Figure 5. Effect of curing time on the compressive strength of concrete with incorporated MSS/MSSA as a partial substitute for cement

65x34mm (300 x 300 DPI)

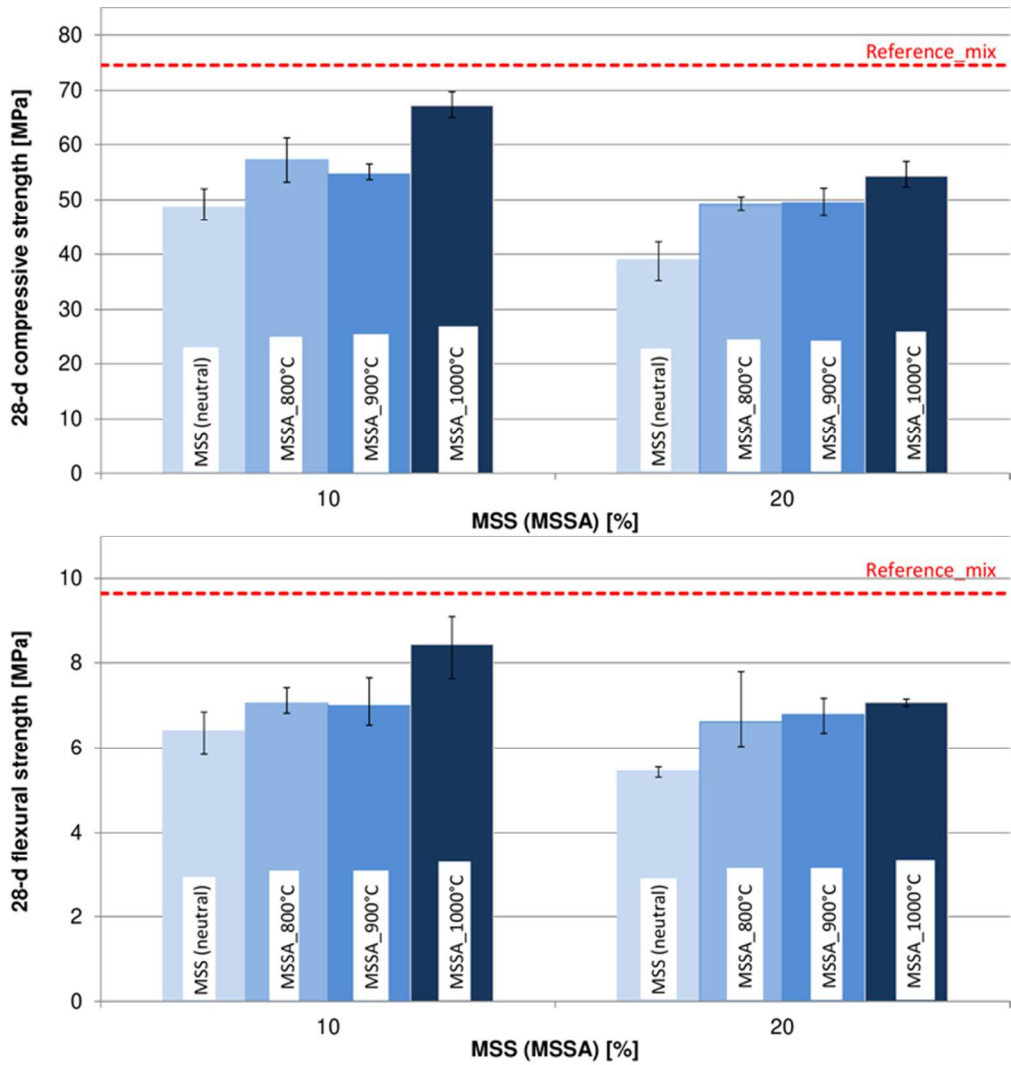


Figure 6. Compressive and flexural strengths of mortar for age of 28-days depending on the proportion and the type of added MSS/MSSA

65x68mm (300 x 300 DPI)

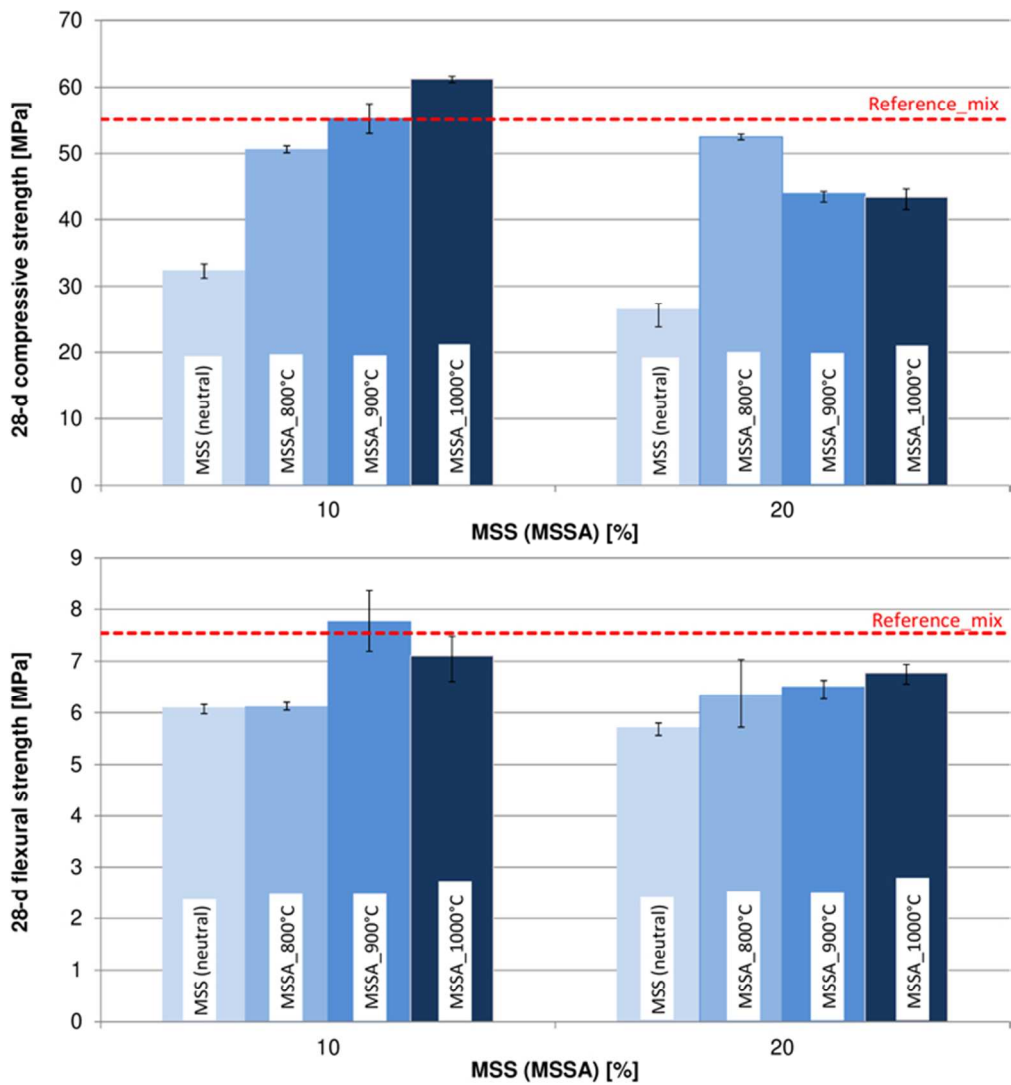


Figure 7. Compressive and flexural strengths of concrete for age of 28-days depending on the proportion and the type of added MSS/MSSA

65x70mm (300 x 300 DPI)

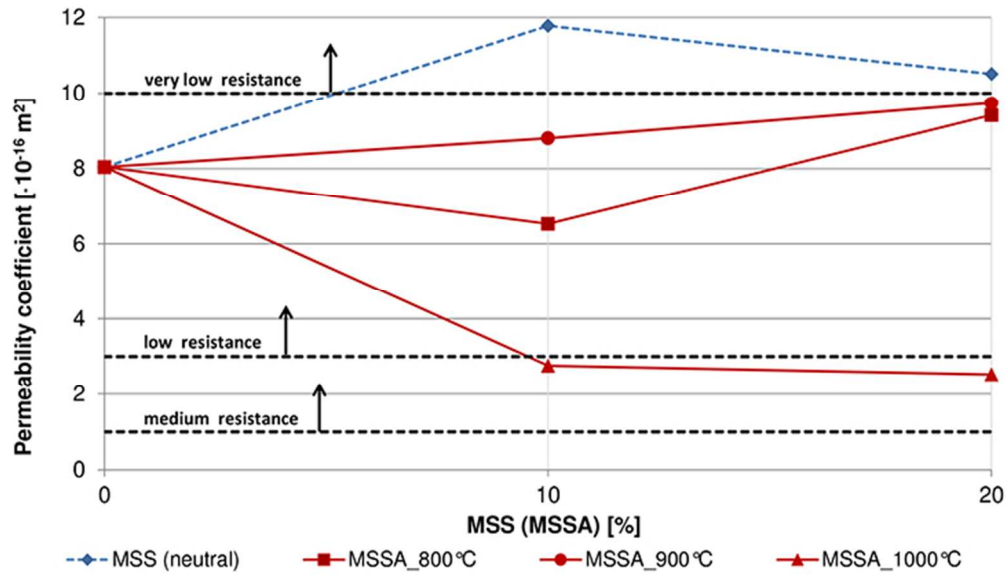


Figure 8. Gas permeability coefficient of mortars depending on the proportion and the type of added MSS/MSSA

61x34mm (300 x 300 DPI)

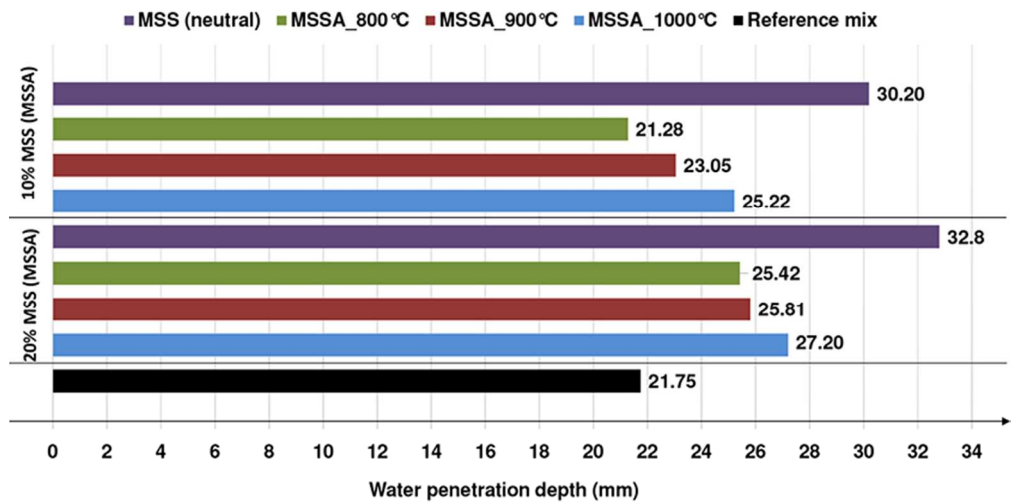


Figure 9. Water penetration depth of concrete depending on the proportion and the type of added MSS/MSSA

70x34mm (300 x 300 DPI)

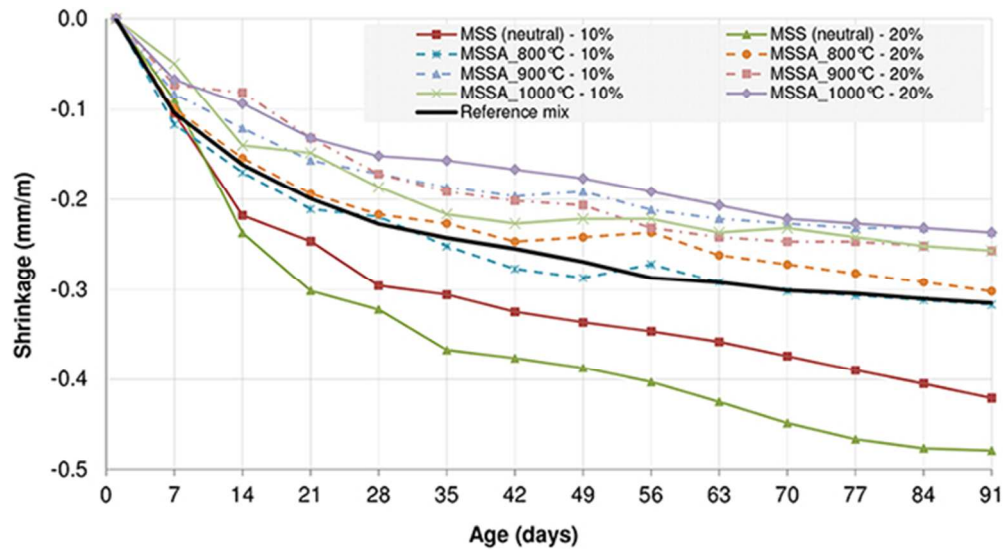


Figure 10. Shrinkage of concrete depending on the proportion and the type of added MSS/MSSA

55x29mm (300 x 300 DPI)

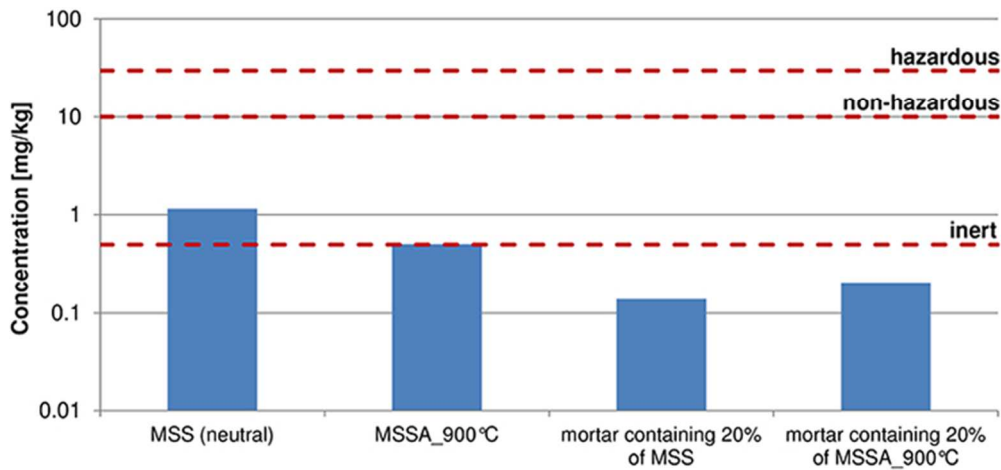


Figure 11. Leaching concentrations of Mo and their comparison with relevant WAC limits for European landfills

62x29mm (300 x 300 DPI)