Aurubis iron-silicate fines: universal sustainable construction material: a state-of-the-art review

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Abstract. This article brings together a lot of research information that deals with iron-silicate fines (ISF), as a basic by-product produced by the copper plant of Aurubis, located in Bulgaria. As a rare material, produced only in couple of plants in the world, ISF has a wide variety of applications due to its specific physical, chemical and mechanical characteristics. Well known for decades by the clinker cements industry, nowadays Aurubis presents a wide variety of new perspectives for creating green and sustainable building materials out of ISF. Sustainability in the construction sector is mostly referred to as zero waste scenarios related to the use of recycled and secondary materials (RSM). Such RSM materials differ significantly and their performance remains to be established separately as well as the properties of the construction products produced by them. Besides this each production unit has its own experience with raw materials for its production and introducing a new one is always causing some initial doubts. ISF not only covers preliminary expectations but even exceeds them. One of the main purposes of this article is to present opportunities to academics, researchers, design engineers, research and development & production managers in companies, specialists and contractors, for sustainable building products development of this not so well-known material with great potential. Most of the presented applications are prepared on industrial scale with different percentages of ISF for testing the effect of its quantity on the properties of the final products.

1. Introduction or what is iron-silicate fines?
Iron-silicate fines (ISF) is a by-product obtained after flotation of smelted copper slag in the plant of Aurubis located in Bulgaria. The main difference between ISF and other iron-silicates produced worldwide is the grain size. Bigger grain size gives bigger advantages in finding the right applications than smaller one. Although other copper slags are mostly cast in pots, followed by air-cooling and crushing up to the desired grain size, or water-quenching, ISF is formed by consecutively cooling the pots, crushing, milling and floating, as a final step of copper extraction. The type of slag treatment is responsible for the microstructural phases, but the chemical composition depends mostly on the initial blend collected by the plant.

The annual world copper slag production in 2014 was about 40 million tonnes [1]. More than one third of it is generated in China, about 60% of the total production is in Asia, less than 20% is in Europe and more than 15% is in South and North America [1]. Different standards define copper slags as a safe material from environmental point of view, including it in the green list of non-hazardous materials from Japan through Europe to USA. ISF production accounts for a small amount of the abovementioned percentages, and is produced mainly in Europe, Asia, Japan and South America and its characteristics...
and areas of application are not so well defined. One of the reasons is the absence of standards for copper slag utilization globally, except for some attempts in Korea and Japan. This article is a state-of-the-art review of all different applications discovered in Aurubis Bulgaria.

ISF contains mostly $\text{Fe}_2\text{O}_3$ in the form of fayalite ($\text{Fe}_2\text{SiO}_4$) and magnetite ($\text{Fe}_3\text{O}_4$). Iron is in a hard relationship with silicon, only a small amount is in the form of free Fe, which makes magnetic separation very difficult. Although there are some promising studies in this direction in and outside of Bulgaria. Slag from the smelter is cooled down using two different methods – air-cooling after the pots are discharged and cooling in the pots with water streaming on the top surface. Phase formations are in the same range for both methods: about 35% crystalline phase and 65% amorphous phase. These results differ from those of the other copper slags, which are predominantly crystalline for ordinary air-cooled slags and mostly amorphous for granulated ones. According to many scientists, amorphous structure is responsible for the pozzolanic activity of the final copper slag [2,3]. That is why the glassy structure of the ground granulated blast furnace slag and the fly ash have been facilitating the development of cement and concrete production for decades and have been included in building standards. The different cooling technology of ISF forming 2/3 amorphous structure can make this by-product another sustainable alternative as a cementitious component compared to the other already established materials. The average size of 20 μm can be beneficial for production of cement, mortars, concretes, ceramics and asphalts which require fine grained material. The specific density of the material, based on BNS EN 1097-6, is found to be 3.8 g/cm³, which is close to the densities of 3.91 g/cm³, reported by other copper slag producers [4,5]. Additional information on the physical, chemical and mechanical characteristics of the ISF can be found in [6,7]. Chemical and physical characteristics are constantly maintained.

The goal of the article is to give a wide overview of all established applications of ISF discovered and tested in and out of Bulgaria. The future of this material is in production of green building materials, which is stimulated by the sustainable policy of the EU and the EU Green Dial strategy [8,9].

2. Where is the bottleneck in by-products material application?
Difficulties in direct application of by-products can be divided into two directions: absence of standards and the waste status of the materials. Each application requires defined procedure for its utilization. This procedure is described in standards and normative documents required by the Institutions. In Bulgaria, due to the waste status of the ISF, each company which utilizes ISF must have a permission by the Regional Inspection of the Environment and Waters for its application in their production and must provide regular reports on the quantity of material they have included in their production. For customers outside of Bulgaria the procedure is the same in accordance with the European Waste Directives. The third aspect is the additional technological efforts for implementation of a new material in production, which requires installation and software upgrades.

Despite the abovementioned difficulties, the construction sector in Bulgaria shows willingness to start ISF utilization on a large scale, due to its benefits and the absence or scarcity in Bulgaria of other alternatives defined in the construction standards, such as fly ashes, ground granulated blast furnace slag, pozzolans and silica fume. Together with the EU directives on wider utilization of wastes, ISF can cover this gap for local effective material. Certified as an aggregate by the Declaration of Exploitation Characteristics, the ISF fulfills the criteria for application in concrete.

3. Applications of iron-silicate fines
The engineering characteristics of ISF affect very positively the properties of the final products where it is applied. This paper gives a wide overview of many years of experiments with ISF in completely different areas – from construction (clinker; cement; alkali-activated binders; dry plasters; concrete; ceramics; glass ceramics; glass fibres; asphalts; mineral wool, rubbers and caoutchoucs; soil embankments) through steel production to the mining sector and the coal industry. Application of ISF in construction, as one of the largest global markets, is the most promising area of application.
3.1. Cement production

Ordinary Portland Cement (OPC) production includes first clinker production and then crushing and milling with additives for regulation of the setting time. ISF has been successfully applied in cement clinker production for many decades. This article provides an overview of other applications of ISF not only in clinker, but also in blended cements, as well as alkali-activated binders, which are one of the most published about new types of binders out of all types of slag during the recent years.

3.1.1. Clinker cement

Production of cement clinker requires adjustments of four basic minerals. For the formation of the one of them (Ca$_4$AF) is needed a certain amount of iron. If local clays are poor in iron, it is necessary to increase the iron content using additional material. Fe$_2$O$_3$ drops the melting point and it gives higher strength to the cement, better corrosion resistance, increases the setting time and drops the exothermic reaction. ISF is one of the best materials for this purpose. Moreover, it has lower melting point and reduces the calcination temperature in the kiln during cement clinker production [10]. Because of this, the need of mineralizer is reduced or eliminated [11]. Some authors claim that the performance of the cement is even better than that produced with traditional limestone, clay and mill scale [12]. ISF improves the grindability of the clinker and does not require additional crushing.

3.1.2. Blended cements

Building materials utilized in cement-based products to reduce the level of cement to a certain extent are called ‘Supplementary Cementing Materials’. The pozzolanic properties of copper slags in blended cements have been researched for decades [13, 14, 15]. The potential suitability of copper slag for use as a cementitious component has been examined and its positive effects have been proven. Moreover, studies reported that copper slag does not need to be completely amorphous for a significant hydration process to occur.

It is examined the effect of ISF and 2 different types of fly ashes (FA1 and FA2) substituting 10% and 25% of the cement. Test results show that the mortars prepared using ISF give relatively the same flexural strength at all ages, but the compressive strength differs. The early (2day) and late (3month) compressive strength of those mixtures, which contain ISF, is higher than the compressive strength of those with FA substitution. These results are more obvious at higher percentages of cement substitution (25%). The final strengths at 10% are comparable (>95%) to pure cement mortar. One of the reasons for the lower strength values at higher cement substitution of both FA and ISF is the higher water consumption for one and the same workability. When sand is substituted with ISF, even though the water/cement ratio increases, the compressive strength of the mortar increases by 30%. This means that when appropriate chemical admixture is applied to improve the rheology of the mix, the final strength will be even higher.

3.1.3. Alkali-activated binders

Alkali-activated binders (AAB) have been proclaimed as a real Portland Cement (PC) alternative during recent years. In addition, the use of industrial by-products like fly ash, high furnace slag, blast furnace slags, fayalitic slags, etc, in AAB has been declared the most promising area of their application. This new type of binder can contain a certain amount of PC, but it is not even necessary if the by-product contains enough SiO$_2$ and Al$_2$O$_3$ and has high reactivity with the precursor. Some researchers [16, 17] suggests that AAB have a higher resistance to fire and improved performance at elevated temperatures and even against acids.

Production of AAB from ISF has been proven through activation with potassium silicate. The fayalite phase within the ISF is reactive during alkali activation, and the addition of a small quantity of either PC, ground granulated blast furnace slag, or steel slag, brings advantages in strength development [18]. The properties of fresh mortar made out of AAB have been improved by adding water and chemical admixture. The reaction products formed are not only CSH gel, but also new alumino-silicate hydrates,
made by the combination of the potassium silicate and the CSH gel. Curing conditions also significantly affect the properties of AAB. One of the most interesting applications of ISF in AAB is for anti-skid surfaces (ASC). Additional information can be found in [19].

3.2. Plasters based on different binders
Plasters and different types of coatings and polishes are another huge segment in construction chemistry. They have developed very fast during the past several decades with worldwide trading names having local plants in every country. Most plasters are prepared in sacks and buckets for direct application after adding water (for cement based) or applied in air (for air-hardening). This type of products is fast growing due to its precisely developed composition containing a wide range of materials and chemicals.

3.2.1. Cement plasters
Cement plasters are everywhere around us: inside and outside of buildings, infrastructural facilities, transportation lines, industrial areas, etc. Applied on horizontal and vertical surfaces they need to provide comfortable living and working environment, sustainable construction and effective material resource utilization in changing weather. ISF not only makes plasters more sustainable, but also improves their properties first in fresh state for easier handling and enhance the mechanical characteristics in hardened state for plasters where this is required. ISF give volume and linear stability and decrease shrinkage, which is one of the most important parameters in cement-based plasters.

3.2.2. Polymer plasters
Polymer plasters are made out of a matrix of special types of fillers, bonded together by a polymer to achieve the desired properties. The know-how of the producers of these products is related to choosing the correct type of polymer for different applications in many industries, including marine, aerospace, automotive and electrical. The use of ISF with an average particle size of 20μm as a filler increases the adhesion properties and thermal conductivity of the resultant composites, as proven by Aurubis. In combination with glass-fibres, according to some authors [20], small grain size copper slag like ISF improves flexural and tensile strength, tensile modulus and hardness.

3.3. Concrete production
Application of ISF in concrete can substitute partially cement and/or sand. The following paragraphs discuss ISF as an alternative material to sand. ISF increases the consistency of concrete, but it also retards the setting time. Nevertheless, initial strength is higher than reference mixtures with ordinary sand. The water-cement ratio is adjusted by adding chemical admixtures and thus the final strength and modulus of elasticity are improved. ISF compacts the structure by filling the pore structure both mechanically and chemically, enhancing concrete durability and agent resistivity, improving abrasion and wear resistance. Concretes do not show any shrinkage after 1-year examination and show lower level of heat of hydration. ISF can be implemented in many different types of concrete presented below.

3.3.1. Ready-mixed concrete
Ready-mixed concrete (RMC) is used as a reference for the stage of growth of a unit (city; country; union; continent). ISF can be applied as an aggregate which additionally improves the properties in fresh and hardened state. Due to the small grain size and the limits by the standards ISF cannot be applied in large amounts. Nevertheless, even 50÷100kg/m³ increase compressive strength, especially at early age (2nd and 7th day) and after 90 days. There are two reasons for this: the small grain size of 20microns immediately mechanically compacts the structure at early age, compared to evaporated water and bigger open porosity in ordinary concrete, and the late formation of additional chemical products, which require time for the activation of the reactive amorphous phase, which is followed by additional CSH gel formation. This process is supported by appropriate composition and suitable chemical admixture with cement and ISF. The other great advantage of ISF is that there is no risk of alkali-silica reaction due to the very high thermal treatment of the material and absence of reactive agents.
3.3.2. Concrete products

Vibro-pressed concrete products are widely distributed in urban areas. The technology of their production requires a concrete mix design with specific workability and flowability of the fresh concrete mix and at the same time high mechanical properties and durability of the hardened products. ISF, which in general improves the properties of hardened concrete, is effectively utilized in paving products by covering the requirements for low water-cement ratio and formability of elements. ISF can be used for a wide range of concrete products like tiles, blocks, panels, curbs, etc. One of the greatest benefits of ISF application in concrete products is the improvement of mechanical properties by more than 25%. Additional information can be found in [7].

3.3.3. Special concretes

There is a wide range of special concretes, but here we will focus on those, in which the use of IFS can have special benefits due to its physical and chemical characteristics.

3.3.3.1. Heavy-weight concrete

Heavyweight concrete is a material which mostly uses aggregates like barite and magnetite, which are rare in Bulgaria. Heavyweight concretes are used where high density and heavy weight required by standards. BNS EN 206 defines heavyweight concrete as a material which has an oven dry density of more than 2600kg/m$^3$. The specific density of ISF is about 3700kg/m$^3$, which is about 50% higher than ordinary aggregates used in construction, higher volume of chemical admixtures and the same cement and water/cement ratios for the desired strength class. According to detailed Laboratory tests by Aurubis (both mechanical and durability) heavyweight concrete with ISF can be applied into: heavy foundations for special structures; underground and tunneling facilities; marine structures (coast protection, retaining walls, tetrapods); bridges; anchorages; backfilling of pipelines, LegoBlocks, etc. Improved durability, especially waterproofing (Cw0.8 & Cd50 (BNS EN 206:2013 & NA.N)) and protection against the aggressive impact of chlorides, sulphates and salts in a combination with increased frost resistance, abrasion resistance and volume stability make it a perfect material for all these uses.

3.3.3.2. Radioactive concrete

ISF shielding concrete is a building material used for the construction of protection shields. These shields guarantee the work safety of the people inside the structures, subjected to different types of radiation and attacks. This type of concrete is used for: walls, ceilings and floors against ionizing radiation; multi-threat protection from electromagnetic radiation; radiation protection in hospitals, laboratories, oncology clinics and waste treatment facilities; protection against the hazard of nuclear radiation leakage; protection against terrorist attacks and protection against extreme natural disasters. The high density of ISF and its small grain size compact the structure and make it resistant to external attacks.

3.3.3.3. Ultra high performance concrete

Ultra High Performance Concrete (UHPC) is characterized by a very high compressive strength (above 150 MPa) and extreme durability, even when exposed to highly aggressive environmental impacts. All these characteristics make it an alternative to other construction materials (e.g. steel) for the construction of transport and hydraulic facilities, high-rise buildings, as well as for special mine structures, structures for military application and high aesthetic architectural elements and details. ISF is one of the best materials for making UHPC, which brings plenty of benefits in the structures and elements starting from micro- and macro- structural optimization, improving workability and creating long-lasting products. Aurubis has developed UHPC products with high aesthetic vision for outdoor application.

3.3.3.4. De-icing concrete

De-icing concrete is a special mixture containing ingredients, which are electrically conductive. Ordinary concrete does not have this property. The composition of de-icing concrete consists of high
quantities of ISF in combination with other geological materials with high iron content and a cocktail of building materials. When de-icing concrete is connected to a power source, its ingredients are heated and prevent ice formation on the concrete surface. This special type of concrete is used on several US bridges and sidewalks and was invented by Prof. Christopher Tuan and assigned by the University of Nebraska with Patent No.: US 6,825,444 B1 [21]. The concrete surface is heated up to +20° Celsius above the ambient temperature with minimum electrical supply. Aurubis applied a sidewalk in its plant in order to prove the electroconductive properties of ISF and successfully melts snow during the winter period.

3.4. Asphalt mixtures
Asphalt mixtures are mixtures that combine different grain size aggregates bound by bitumen. Mineral filler is one of the important aggregates, because it not only fills voids in mixes, but also improves the cohesion of the asphalt binder. The most frequently used type of filler is limestone powder, containing over 90% of CaCO$_3$, together with waste materials from crushing coarse aggregates. ISF, as extremely fine aggregate, is successfully applied in asphalt mixtures, once it is dried. Due to its large specific surface (about 0,92m$^2$/g), ISF sticks on the bitumen and increases the specific surface of the binder by itself by creating better cohesion with the other coarser aggregates. As a result, the compactness of the mixtures is increased and the void content is reduced, which is important for the lifetime of the asphalt layer and its durability. ISF also improves the Marshall’s stability and the Marshall flow test results.

3.5. Ceramic products
Ceramic is one of the most ancient building materials on our planet, dating from earlier than 10 000 years BC. Nowadays, scientists and the industry have been testing a wide range of alternative materials for ceramic production, which improve the properties of the final products on the one hand, reduce the extraction of natural resources on the other and drop energy consumption in total. ISF is a material, which utilization leads to several benefits in different types of ceramic products (bricks, ceramic and clinker tiles & plates, roof tiles, etc.). Aurubis investigations in this direction show that the use of ISF contributes greatly to the ceramic products’ properties both is plastic and hardened state. ISF first improves the plasticity of the clay by decreasing the decomposition of the clay, then decreases plasticity during drying and linear shrinkage, followed by increasing the compressive strength of the products and improving their thermal and sound insulation capacity and acid resistance. Moreover, due to the high iron content in ISF, which is threatened at high temperatures during copper extraction, the sintering temperature drops and therefore the energy consumption is reduced. The application of ISF in ceramics has great potential.

3.6. Other applications
The other possible applications of ISF are also interesting and can be implemented in large scale if ISF covers the requirements of the final customers in respect to their production peculiarities.

3.6.1. Soil embankments and stabilization
ISF is a product that has been tested in-situ in combination with soil for different applications to enhance the physical and mechanical properties of the soil. ISF increases the shear strength and can control the shrinkage and swelling properties. This improves the load bearing capacity of the subgrade of roads and other types of construction works. According to the type of soil and application different percentage of ISF can be applied for stabilization of the soil.

3.6.2. Mineral and glass wool
The incorporation of slags, mainly blast furnace and steel slags, in mineral (or stone) wool production is not a new practice. The goal of their utilization, besides the environmental aspect, is lowering the melting temperature and supporting the flow of the molten rock. ISF can efficiently do the same, as the iron component is much higher compared with the slags from the ferrous industry. Mineral wool
production utilizes about 25% by-products in the total mix and 10% off-cuts from the plants’ own production process. Each company has its own requirements, mostly related to chemical composition to keep the flux, solid content to act as a fuel and particle size to avoid interference with the kiln operation. Copper slags are successfully applied in USA for mineral wool production.

Glass wool utilises a high percentage of post-consumer recycled glass as recycled content. Industrial by-products are also recycled to a limited extent, because the slightest variation in feedstock composition can affect the fibre length of the product.

3.6.3. Glass ceramics and glass fibre
Iron-rich phases of copper slag impart magnetic, electrical and thermal properties, as well as a brownish shade to glass-ceramics [22]. Each copper slag, based on its specific chemical composition and percentage of clay substitution, must be examined for its sintering peaks in a range between 750°C and 1100°C. According to some researchers [23, 24] the optimum values for high density and hardness in a combination with low porosity and water absorption were discovered at 950°C with 61.5% copper slag. Other researchers [25] achieved the best properties after sintering at 1025°C for 1 hour. The tiles have a bending strength of 57 MPa, 2wt% water absorption and excellent resistance to mineral acids, suitable for production of chemical resistant floor tiles. ISF addition in glass ceramics leads to an unusual sintering process in low temperature internals between 1150°C and 1200°C. These temperatures provide significant technological advantages such as great reduction of the firing shrinkage, as well as low porosity and high crystallinity, followed by good mechanical characteristics of the final products. Another interesting application of copper, which has been reported by [26] is for glass fiber production.

3.6.4. Rubbers and caoutchoucs
Fillers are the second most important component in rubber and caoutchouc composites by volume used. These additives are commonly used either as diluents, process improvers, aesthetic improvers or as reinforcers. Like fillers in asphalts, here they are used to reduce the polymeric matrix and to reinforce the composite by physical and chemical interactions. The fine grain size, high specific surface area, structure and density of the ISF make its application beneficial. The complex interactions allow material flexibility to be maintained, while enhancing strength and resistance to deformation. ISF with moisture content below 1% has been successfully tested in production of heavy rubbers.

4. Conclusion
The following article gives a wide overview of ISF application in more than 15 different directions. This is the first detailed presentation of this kind of special copper slag produced only in a couple of plants in the world. The article gives summarized information of the several years of investigations made by Aurubis. Material peculiarities, together with absence of EU standards do not discourage Aurubis from finding new directions for its product. On the contrary, these peculiarities make it more attractive, more interesting and, since it is available in Bulgaria, it fulfils the criteria of the EU commission for sustainable utilization of by-products, as prescribed by the Green Deal of construction products producers. In this respect, ISF, with its constant chemical composition and physical properties, can maintain the high quality of products and support producers in making their industries greener.

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