Treatment and utilization of artificial aggregate in the production of cement composites

R Papesch¹, K Macalova², J Charvat², T Dvorsky² and V Vaclavik²

¹The Technical and Test Institute for Construction Prague, branch Ostrava.
²VSB - Technical University of Ostrava, Faculty of Mining and Geology, Department of Environmental Engineering, Czech Republic

Abstract. The aim of the work is to find a suitable way of treatment of steel ladle slag for subsequent use as a partial replacement of the binder component in cement composites. The goal is based on the raw materials policy of the Czech Republic. Within this work is solved the issue of possible use of steel slag as the largest by-product of steel production. The work is focused on a specific ladle slag from ladle furnaces, by which are equipped the modern steel plants. Ladle slag is similar in chemical composition to Portland cement. However, its mineralogical composition should be taken into account in relation to its expansion reactions and lower hydraulic activity. One of the goals is the research of effect of particle size in cement-slagger mixtures. The slag was ground for research on two different specific surfaces - coarsely in a vibrating mill and finely in a ball mill. The research within the experimental part of the work verified the positive influence of ladle slag on the properties of fresh and hardened mortar mixtures. Tensile bending strengths and compressive strengths are for some mixtures with ladle slag even higher than the strengths of the reference mixtures.

1. Introduction
In recent years, emphasis has been placed on promoting recycling and increasing the use of secondary resources, especially with regard to environmental protection [1-3]. The essence is in efficient and sustainable provision and use of ore, energy or construction resources. The main vision of the strategic document "Policy of Secondary Raw Materials of the Czech Republic" is the modification of waste into resources. The main intention in the field of building materials is the maximum possible use of local products. For the ecological and economical acceptance of projects, is necessary when raw materials of sufficient quality are available as close as possible to the place of construction. The necessary precondition is that the obtained secondary raw materials comply with technical standards which meets the strict requirements imposed on primary materials [4]. The mining, power and metallurgical industry have the largest contribution of secondary raw materials.

The main goal of this work is to find a suitable method of treatment of ladle slag for subsequent use as a partial replacement of the binder component in cement composites. This goal is based on the raw materials policy of the Czech Republic, with its main goal in:
- the increasing self-sufficiency of the Czech Republic in raw material resources by substituting primary sources by secondary materials,
- support of innovation ensuring the recovery of secondary materials in a quality suitable for further use in industry,
- support of the use of secondary materials as a tool for reducing the material demands of industrial production,
The work deals the issue of possible use of steel slag as the largest by-product of steel production. The work is focused on a specific slag from ladle furnaces by which are equipped the modern steel plants. Ladle slag is in chemical composition similar to Portland cement. However, its mineralogical composition must be taken into account in relation to expansion reactions and lower hydraulic activity. One of the goals is the research of the effect of particle size in cement-slag mixtures. The research is related to slag of Třinecké železárny, fraction 0/8 mm, which was ground to two different specific surfaces - coarsely in a vibrating mill and finely in a ball mill. The experimental part of the work deals with the verification of the possible use of slag as a partial replacement of cements in cement composites.

2. Product of secondary metallurgy - Slag

Slags are a by-product of combustion and thermal processes. These are accompanying products of metallurgical production. They are formed by melting ore tailings, slag-forming substances and minerals. Slag plays an essential role in the production and melting of metals by providing heat exchange between furnace-metal. The chemical composition of slag varies with regard to the type of produced steel, the composition of ores, flux, and coke (Cao 30-50 %, SiO₂ 25-35 %, Al₂O₃ 7-25 %, MgO 1-17 %). Slags, similarly as cements, are judged by so-called modules.

Alkalinity module – ratio between basic and acid oxides expressed in % by weight. Based on the result, the slag is used as an aggregate to concrete (Mₔ <1, acid slag) or for cement purposes (Mₔ> 1, basic slag) [5]. See eq. (1).

\[ M_\gamma = \frac{CaO + MgO}{SiO_2 + Al_2O_3} \]  

(1)

The effect of CaS and MnO, which are described by the index F, is also taken into account. See eq. (2).

\[ F = \frac{CaO + CaS + 0.5MgO + Al_2O_3}{SiO_2 + MnO} \]  

(2)

At F < 1 slag is unsuitable for cements
At F = 1 – 1.5 average slag
At F = 1.5 – 1.9 slag in good quality
At F > 1.9 slag of the highest quality [6]

Due to the form of MgO, its high level is not desirable because it does not have hydraulic properties. Between accessory components belongs TiO₂. At higher volumes of MnO (above 3 %) there is a decrease in hydraulic activity [7].

2.1 Ladle slag

This type of slag consists of slag-forming additives added during slag tapping and those added during steel processing. Modern steel plants currently use ladle furnaces as a part of secondary production process. The ladle furnace is used for the production of high-quality pure steel of high metallurgical quality and useful properties.

The main task of ladle furnaces is to achieve deep desulphurisation of steel using refining slag. The treatment of the metal takes about 30 minutes and it is possible to achieve desulfurization up to 0.003 % S [8].
Characteristics of ladle slag:
The basic minerals are $\text{C}_2\text{S}$, $\text{C}_3\text{S}$ or $\text{C}_4\text{AF}$. Ladle slag is one of the types of converter steel slag characterized by a high content of calcium oxide $\text{CaO}$. It is basic slag and reducing slag [9]. As far as the ladle slag, its possible volume instability must be taken into account [10]. The volume stability depends on the free lime content. Free lime occurs in ladle slag in two types, it is residual free lime from the raw material and precipitated lime from molten slag. Stability problems are mainly caused by residual lime. It is also noteworthy that the free lime content increases with increasing alkalinity of the slag [11]. The relation between the residual lime, the precipitated lime and the total free lime content in steel ladle slag is shown in Fig. 1.

![Figure 1. Relation between residual lime, precipitated lime and total free lime content in steel ladle slag [11].](image)

The chemical composition of slag from the ladle furnace of Třinecké železáry is given in Tab. 1.

|     | Fe  | FeO | SiO$_2$ | Al$_2$O$_3$ | MnO | CaO | MgO | P$_2$O$_5$ | S     | Cr$_2$O$_3$ | TiO$_2$ | Zn   | P$_2$ |
|-----|-----|-----|---------|-------------|-----|-----|-----|------------|-------|-------------|---------|------|------|
| Max.| 6.7 | 0.0 | 40.9    | 40.9        | 17.7| 63.1| 17.3| 0.6        | 3.75  | 2.1         | 1.7     | 0.024| 3.1  |
| Min.| 0.1 | 0.0 | 2.6     | 1.7         | 0.0 | 28.4| 2.8 | 0.0        | 0.0   | 0.0         | 0.0     | 0.001| 0.7  |
| ø   | 1.2 | 0.0 | 21.9    | 11.9        | 1.6 | 47.3| 6.4 | 0.0        | 0.3   | 0.0         | 0.4     | 0.003| 1.7  |

2.2 Methodology of performed tests
The tests of physical-chemical and physical-mechanical properties for input raw materials and fresh and hardened mortar mixtures were performed in accordance with below stated standards.

Determination of setting times in accordance with EN 196-3 [12].
Determination of specific weight in accordance with ČSN 72 2113 [13].
Determination of specific surface in accordance with EN 196-6, cl. 4 [14].
Determination of particle size distribution by sieving method in accordance with EN 933-1 [15].
Determination of consistence of fresh mortar in accordance with EN 1015-3 [16].
Determination of absorptivity after 28 days in accordance with ČSN 73 1316 [17].
Determination of thermal conductivity coefficient after 28 days in accordance with EN 12667 [18].
Determination of flexural and compressive strength of hardened mortar in accordance with EN 1015-11 [19].
3. Experimental part

3.1 Input raw materials
Cement CEM I 42.5 R / Cement CEM III/A 42.5 N (manufactured by company Cement Hranice).
Ladle slag (coarsely ground with grinding time 5 minutes in vibrating mill / finely ground with grinding time 45 minutes in ball mill).
CEN-NORM sand in accordance with standard EN 196-1 (manufactured by company Filtrační písky).
Tap water of temperature 21 °C.
Description of physical-chemical properties and granulometry of input raw materials is stated below in table 3 and 4.

3.2 Recipes of slag-cement mixtures
The aim of this part of the work was to verify the properties of fresh and hardened mortar mixture with 10, 20 and 30 percentage of finely or coarsely ground ladle slag of Třinecké železárny instead of cement. We were mainly interested in the influence on physical-mechanical or physical-chemical properties, which would allow the use of a larger proportion of slag in cements and thus increase the possibility of using these secondary products from steel production.

| Type of mixture | Type of Cement CEM I / CEM III | Type of ladle slag / Fineness of grinding (Coarse / Fine) | Sand [g] | Tap water [g] |
|----------------|-------------------------------|--------------------------------------------------|---------|--------------|
| R1             | 450                           | 0                                                | 1350    | 225          |
| R2             | 405                           | CEM I                                           | 1350    | 225          |
| R3             | 360                           | 42.5 R                                          | 1350    | 225          |
| R4             | 315                           |                                                | 1350    | 225          |
| R5             | 450                           | 45                                              | 1350    | 225          |
| R6             | 405                           | CEM III/A                                       | 1350    | 225          |
| R7             | 360                           | 42.5 N                                          | 1350    | 225          |
| R8             | 315                           |                                                | 1350    | 225          |
| R9             | 450                           | 0                                               | 1350    | 225          |
| R10            | 405                           | CEM I                                           | 1350    | 225          |
| R11            | 360                           | 42.5 R                                          | 1350    | 225          |
| R12            | 315                           |                                                | 1350    | 225          |
| R13            | 450                           | 0                                               | 1350    | 225          |
| R14            | 405                           | CEM III/A                                       | 1350    | 225          |
| R15            | 360                           | 42.5 N                                          | 1350    | 225          |
| R16            | 315                           |                                                | 1350    | 225          |

3.3 Determination of physical-chemical properties of input raw materials

| Type of input raw material | Initial setting time [min.] | Final setting time [min.] | Setting time [min.] | Amount of water [% wt] | Specific surface [cm²·g⁻¹] | Density [g·cm⁻³] |
|----------------------------|-----------------------------|---------------------------|---------------------|------------------------|--------------------------|-----------------|
| CEM I 42.5 R               | 180                         | 205                       | 25                  | 26.6                   | 3670                     | 3.13            |
| CEM III/A 42.5 N           | 210                         | 250                       | 40                  | 28.0                   | 3785                     | 3.01            |
Table 4. Overview of granulometry of input raw materials.

| Type of input raw material | Sieve mesh [mm] / Sieve residue [g] | \(d_{50}\) [mm] |
|---------------------------|-------------------------------------|-----------------|
|                           | 2    1   0.5 0.25 0.125 0.063    | Undersize product |
| CEM I 42.5 R              | 0    0   0    48.5 215.6 120.5 | 14.9            |
| CEM III/A 42.5 N          | 0    0   0    1.5  255.5 115.4 | 24.6            |
| Coarse ladle slag         | 4.1  15.8 57.4 64.8 81.3 111.3 | 65.0            |
| Fine ladle slag           | 0.2  0.3  6.2 64.6 190.5 93.1  | 44.1            |

The above results show a very short setting time for coarsely ground slag. On the contrary, in the case of fine slag, the setting time was significantly prolonged. For cements, the results confirmed generally known setting times. Regarding the determination of the granulometry of the input raw materials, the calculated mean grain size \(d_{50}\) was almost identical for all raw materials (0.15 - 0.16) mm.

3.4 Determination of physical-mechanical properties of slag-cement mixtures

Determination of consistency of fresh mortar

Table 5. Consistency of mixtures with coarse ladle slag.

| Type of mixture | Fineness of grinding | Consistency of fresh mortar | \(\varnothing\) [mm] | Increase [%] |
|-----------------|----------------------|----------------------------|-------------------|--------------|
|                 |                      | The value of spillage [mm] |                   |              |
| R1              | Coarse               | 16.3                       | 16.3              | -            |
| R2              |                      | 18.5                       | 18.0              | 12.26        |
| R3              |                      | 18.5                       | 18.0              | 12.26        |
| R4              |                      | 18.6                       | 18.0              | 12.26        |
| R5              |                      | 19.7                       | 19.2              | -            |
| R6              |                      | 19.8                       | 19.7              | 1.54         |
| R7              |                      | 20.0                       | 19.7              | 2.05         |
| R8              |                      | 20.6                       | 19.8              | 3.59         |

Table 6. Consistency of mixtures with fine ladle slag.

| Type of mixture | Fineness of grinding | Consistency of fresh mortar | \(\varnothing\) [mm] | Increase / decrease [%] |
|-----------------|----------------------|----------------------------|-------------------|-------------------------|
|                 |                      | The value of spillage [mm] |                   |                         |
| R9              | Fine                 | 16.3                       | 16.3              | -                       |
| R10             |                      | 17.3                       | 17.0              | 5.52                    |
| R11             |                      | 17.5                       | 17.0              | 6.13                    |
| R12             |                      | 17.8                       | 17.2              | 7.36                    |
The mixtures with Portland cement, with slag shares, showed significantly improved consistency over the reference sample. The results also show the effect of fineness of grinding on consistency. The increasing fineness decreases the consistency of the mixtures. Mixtures with cement type CEM III/A and fine slag shares have even deteriorated consistency compared to the reference sample.

**Determination of setting times**

| Type of mixture | Fineness of grinding | Settlement [mm] | Initial setting time [HH:MM:SS] | Final setting time [HH:MM:SS] | Amount of water [g] |
|-----------------|---------------------|-----------------|---------------------------------|-----------------------------|-------------------|
| R1              | Coarse              | 8               | 03:12:19                        | 4:31:37                     | 131               |
| R2              | Coarse              | 4               | 03:48:26                        | 04:52:14                    | 128               |
| R3              | Coarse              | 4               | 03:37:07                        | 05:00:40                    | 121               |
| R4              | Coarse              | 4               | 4:12:22                         | 04:53:05                    | 118               |
| R5              | Coarse              | 5               | 04:53:46                        | 06:10:12                    | 139               |
| R6              | Coarse              | 5               | 04:53:55                        | 06:16:23                    | 144               |
| R7              | Coarse              | 4               | 04:53:55                        | Final setting time was not reached* | 133               |
| R8              | Coarse              | 4               | 04:49:34                        | 06:14:00                    | 125               |

* The maximum possible time for determining the end of solidification was 7 hours and 30 minutes.

| Type of mixture | Fineness of grinding | Settlement [mm] | Initial setting time [HH:MM:SS] | Final setting time [HH:MM:SS] | Amount of water [g] |
|-----------------|---------------------|-----------------|---------------------------------|-----------------------------|-------------------|
| R9              | Fine                | 8               | 03:12:19                        | 4:31:37                     | 131               |
| R10             | Fine                | 7               | 4:15:17                         | 06:19:45                    | 131               |
| R11             | Fine                | 8               | 04:14:25                        | 04:39:43                    | 126               |
| R12             | Fine                | 8               | 03:44:21                        | 04:16:23                    | 125               |
| R13             | Fine                | 8               | 03:11:33                        | 06:26:10                    | 140               |
| R14             | Fine                | 4               | 04:46:36                        | 06:31:26                    | 146               |
| R15             | Fine                | 8               | 05:19:06                        | 06:26:10                    | 140               |
| R16             | Fine                | 8               | 05:04:20                        | 06:14:00                    | 134               |

The test results of all mixtures show the effect of slag on the prolongation of setting times (the beginning and the end of solidification) in comparison with reference samples. As the proportion of slag increase, the setting times increase.

**Determination of water absorption for mixtures after 28 days**
Figure 2. Determination of water absorption for mixtures after 28 days.

The comparison of the absorption for individual mixtures is shown in figure above. Mixtures with fine slag shares have a higher but very similar absorption as mixtures with coarse slag shares. Mixtures with slag shares have a higher but very similar absorption as reference mixtures. In general, we can say that the absorption was not significantly affected and ranged between 8 and 9 percent for all mixtures.

Determination of thermal conductivity coefficient \( \lambda \) after 28 days

Table 9. Thermal conductivity coefficients \( \lambda \) of selected mixtures.

| Type of mixture | Fineness of grinding | Thermal conductivity coefficient \( \lambda \) [W·m\(^{-1}\)·K\(^{-1}\)] | Sample thickness \( d \) [mm] | Thermal resistance * \( R \) [m\(^2\)·K·W\(^{-1}\)] |
|-----------------|---------------------|-----------------------------|----------------|---------------------|
| R1              | Coarse              | 0.1025                      | 25.203         | 0.24588             |
| R4              | Coarse              | 0.1161                      | 28.543         | 0.24584             |
| R5              | Coarse              | 0.0989                      | 24.308         | 0.24583             |
| R8              | Coarse              | 0.1070                      | 26.295         | 0.24575             |

\*\( R = \frac{d}{\lambda} \).

Mixtures with 30% part of coarse-grained ladle slag did not have worse results of thermal conductivity to the reference mixture.

Determination of tensile bending strengths after 2, 7, 28 and 90 days

Figure 3. Coarse-grained ladle slag + CEM I 42.5 R.

Figure 4. Fine-grained ladle slag + CEM I 42.5 R.
The graphs for recipes with Portland cement and ladle slag shares show a faster onset of initial strengths compared to blast furnace cements. However, for long-term strengths, mixtures with CEM I and CEM III and a 10% share of coarse slag already reached the minimum strength values required by the cement class 42.5 MPa. After 28 days, all mixtures with fine slag and CEM I showed a significant increase in strength compared to mixtures with coarse slag. The mixture with a 10% share of fine slag showed even higher values compared to the values of the reference mixture. All mixtures with fine slag after 28 days met the minimum strength values required by class 42.5. For CEM III cement, this value was met only by mixtures with a 10% share of fine and coarse slag. For mixtures with shares of fine slags, after lower initial strengths, an increase in long-term strengths is noticeable.
4. Conclusion
The current research within the experimental part of the work verified the influence of ladle slag on the properties of fresh and hardened mortar mixtures. Based on the results of the experiment, the following conclusions can be drawn:
- Coarsely ground ladle slag has very fast setting times, with increasing fineness of grinding the setting times are significantly longer,
- The specific surface of the ground ladle slag can be adjusted depending on the length of grinding and the type of grinding device (according to need 2000-7000 cm²·g⁻¹),
- The specific weight of coarse and fine ladle slag is the same and slightly higher than for cements,
- The amount of water to achieve the required consistency (the spillage value) increases significantly with the fineness of the slag,
- For all mixtures with shares of coarse slag we can say that the slag improves the consistency compared to the reference mixture,
- The mean grain size $d_{50}$ was the same for all input raw materials (0.15-0.16) mm,
- Ladle slag has a prolonging effect on the setting times of all mixtures (meant for the first 10 hours after mixing together the input raw materials),
- For all mixtures with slag contents, the absorption capacity of hardened mixtures after 28 days is not affected,
- Ladle slag do not have a negative effect on thermal conductivity and thermal resistance ($\lambda$ values are the same as for reference mixture),
- Tensile bending strengths and compressive strengths are for some mixtures with ladle slag shares lower, equal or even higher than the strengths of the reference mixtures,
- Half of all mixtures meet the requirement to achieve a minimum value of compressive strength after 28 days of 42.5 MPa (mostly the mixtures with shares of fine slag),
- Replacement of cements CEM I and CEM III with shares of ground ladle slag is possible.

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[13] ČSN 72 2113 Determination of specific weight for cement

[14] EN 196-6, cl. 4 Methods of testing cement - Part 6: Determination of fineness

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[17] ČSN 73 1316 Determination of moisture content, absorptivity and capillarity of concrete

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