Ferromolybdenum slag as valuable resource material for the production of concrete blocks

Boehme L., Van Den Hende D.
Outline

- Introduction
- Production process
- Materials in use
- FeMo-slag
- Mix design
- Properties of ‘R-blocks’
- Bringing the product to the market
- Conclusions
Introduction

- Dirk Van Den Hende
  - Van Den Hende Beton N.V.
  - Concrete products: blocks, pavement, garden,...

- Luc Boehme
  - Catholic University College of Bruges & Ostend
  - Faculty of Engineering Technology - Department of Construction
  - Head of Department
  - Promoter of the research-group “Recycling of C&DW”

- Idea based on former research project “recyMblock”
Recycling slag in building materials

Case:
- Concrete blocks
- Natural aggregates
  - become scarce
  - expensive
- Substitute for gravel and limestone: secondary aggregates
e.g. recycled concrete aggregates and slags
Benefits from using secondary aggregates
- Less expensive
- Reduction of the amount of waste

Flemish environmental law: ‘VLAREA’
Sustainable development: saving ecosystems
Various by-products can be used
Various by-products can be used in concrete blocks

Mixed construction and demolition waste (Boehme L)

Crushed clay brick (Poon et al)

Bottom ashes and granulated blast furnace slags (Yüksel & Bilir)

Recycled concrete aggregates (Pimienta P et al)
Effective use of recycled resources in concrete = reducing harmful effects on the environment

Not valuable solid wastes become valuable alternative to virgin aggregates

Possible effects that can cause deterioration of the end-product must be investigated.

In this case: use of ferromolybdenum slag in concrete blocks for masonry work
Concrete blocks

- Apparent density: 1350 to 1750 kg/m³
- With cavities or full
- High percentage of fine aggregates
- Low percentage of water and gravel
- Low dosage of cement compared to ordinary fresh concrete
- Dry, stiff mixture
Production process

1. Batching and mixing
2. Molding and curing
3. Storage and transportation
Production of concrete blocks

- Schematic overview
Classic raw materials

- Cement
  - Considerations
    - High early strength needed
      → rapid hardening CEM I-type
    - Resistant to certain chemicals (sulphates, chlorides, ..) and ASR
      → CEM III - type
Materials

Classic raw materials

- Sand
  - Riverbeds
    - round shape
    - Upstream: little or no fines; max 5mm
    - Downstream: fine; 1mm
  - Sea → fine & edged
  - Quarry → fine sand + lot of filler

- Aggregates
  - Same sources
  - Larger particle size → 2mm up to 16mm (mostly max 8mm)
Ferromolybdenum slag

Ferromolybdenum
- alloy of iron & molybdenum
- primarily used as additive in steel production (steel, cast irons, nonferrous)

FeMo-slag
- not expected to be hazardous
- in Flanders: 20,000 to 25,000 t/y
- granulated fraction used in concrete: 14,330 to 19,500 t/y
- (CDW: 9,441,000 t/y; steel slag 1,900,000 t/y; nonferrous slag 325,000 t/y; bottom-ashes 310,000 t/y) (VITO)
# Ferromolybdenum slag

## FeMo-slag typical composition

<table>
<thead>
<tr>
<th>Unknown or Variable Composition Substance</th>
<th>Ferromolybdenum Slags</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synonyms/Trade Names</td>
<td>FeMo Slags</td>
</tr>
<tr>
<td>Formula:</td>
<td>By-product obtained during aluminosilicothermic reduction of roasted molybdenite concentrates (tech mo oxide) to produce Ferromolybdenum</td>
</tr>
</tbody>
</table>

### TYPICAL COMPOSITION

<table>
<thead>
<tr>
<th>Parameter / Component</th>
<th>In % (mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>ca. 10 – 40</td>
</tr>
<tr>
<td>Aluminium</td>
<td>ca. 2 – 20</td>
</tr>
<tr>
<td>Iron</td>
<td>ca. 4 – 25</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>ca. 0 – 2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>ca. 0 – 5</td>
</tr>
<tr>
<td>Calcium</td>
<td>ca. 0 – 10</td>
</tr>
</tbody>
</table>

(The REACH Molybdenum Consortium)
Chemical analysis of FeMo-slag used in concrete blocks at VDH jan/08 – nov/10

<table>
<thead>
<tr>
<th>% Mo</th>
<th>% Fe</th>
<th>% Ca</th>
<th>% Al</th>
<th>% Si</th>
<th>% Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>0,12</td>
<td>3,10</td>
<td>3,10</td>
<td>1,90</td>
<td>30,60</td>
</tr>
<tr>
<td>uplim</td>
<td>5,00</td>
<td>20,00</td>
<td>14,00</td>
<td>7,00</td>
<td>38,00</td>
</tr>
<tr>
<td>lowlim</td>
<td>0,00</td>
<td>2,00</td>
<td>2,00</td>
<td>1,00</td>
<td>24,00</td>
</tr>
<tr>
<td>max</td>
<td>0,61</td>
<td>7,50</td>
<td>9,60</td>
<td>3,60</td>
<td>33,30</td>
</tr>
<tr>
<td>mean</td>
<td>0,27</td>
<td>5,40</td>
<td>5,82</td>
<td>2,76</td>
<td>32,06</td>
</tr>
</tbody>
</table>
### FeMo-slag environmental quality

<table>
<thead>
<tr>
<th>mg/kg TDS</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMo</td>
<td>4-15</td>
<td>0.1-0.3</td>
<td>41-799</td>
<td>180-357</td>
<td>&lt;0.2-0.5</td>
<td>49-118</td>
<td>29-129</td>
<td>105-504</td>
</tr>
</tbody>
</table>

(VITO)
Mix design = complex balance

- Different applications $\rightarrow$ other requirements $\rightarrow$ different mixing formulas
- Different aggregates but similar mechanical properties of the blocks

visual result, block quality cost
## Mixing formulas for blocks (wt%)

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>Block for foundation masonry</th>
<th>FeMo-Block for foundation masonry</th>
<th>Block for industrial visual masonry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand 0/1 (quarry)</td>
<td>15%</td>
<td>15%</td>
<td>10%</td>
</tr>
<tr>
<td>Sand 0/2 (sea)</td>
<td>20%</td>
<td>15%</td>
<td>30%</td>
</tr>
<tr>
<td>Sand 0/2 (river)</td>
<td></td>
<td>15%</td>
<td>50%</td>
</tr>
<tr>
<td>Stone 2/4 (quarry)</td>
<td></td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>Stone 4/6.3 (quarry)</td>
<td></td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>Stone 2/6.3 (quarry)</td>
<td></td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>Stone 6.3/14 (quarry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeMo slag</td>
<td>50%</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>Cement CEM I 52,5 N</td>
<td>145 kg/m³</td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>Cement CEM III/A 42,5 N</td>
<td></td>
<td>180 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Cement CEM III/A 52,5 N</td>
<td></td>
<td></td>
<td>180 kg/m³</td>
</tr>
</tbody>
</table>
Mix Design R-blocks

Mixing formulas for R-blocks (with FeMo-slag)

<table>
<thead>
<tr>
<th>Mix Formula standard foundation block</th>
<th>sieve passthrough [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesh [mm]</td>
<td>0/1 qr</td>
</tr>
<tr>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>0.125</td>
<td>7.1</td>
</tr>
<tr>
<td>0.25</td>
<td>81.0</td>
</tr>
<tr>
<td>0.5</td>
<td>97.4</td>
</tr>
<tr>
<td>1</td>
<td>99.1</td>
</tr>
<tr>
<td>2</td>
<td>99.8</td>
</tr>
<tr>
<td>4</td>
<td>100.0</td>
</tr>
<tr>
<td>8</td>
<td>100.0</td>
</tr>
<tr>
<td>16</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mix Formula R-block</th>
<th>sieve passthrough [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesh [mm]</td>
<td>0/1 qr</td>
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<td>8</td>
<td>100.0</td>
</tr>
<tr>
<td>16</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Introduction | Production process | Materials | FeMo-slag | Mix design | Properties of ‘R-blocks’ | to the market | Conclusions

Second International Slag Valorisation Symposium | Boehme L, Van Den Hende D
Mix Design R-blocks

Mixing formulas for R-blocks (with FeMo-slag)

Comparison mix formula standard block & R-block

Sieve pass through [%]

Comparison mix formula standard block & R-block

Sieve pass through [%]

0/1 qr
0/2 sea
2/6,3 qr
6,3/14 qr
FeMo Slag
R-Block
Standard Block
Mixing formulas for R-blocks (with FeMo-slاغ)

- optimal particle size distribution for the mix
- testing the mix in production
  - Influence on distribution of fresh concrete in the mold
  - Influence on compacting the block
  - Visual effects
  - Influence on mechanical properties
  - Influence on W/C-ratio
    - Mechanical properties such as compression strength
    - Stability of the freshly produced blocks
    - Spreading the mixture evenly in the mold

→ fine tuning of the mix
Properties of the R-blocks

**BENOR-certificate**


### Technical Property Description

<table>
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<tr>
<th>Technical Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category of the block</td>
<td>Category I: blocks for load bearing masonry</td>
</tr>
<tr>
<td>Type of masonry</td>
<td>Type C (automatically complies for type D): blocks for foundation masonry (and other indoor masonry)</td>
</tr>
<tr>
<td>(A = outside; B = visual; C = foundation; D = all other)</td>
<td></td>
</tr>
<tr>
<td>Size tolerance class</td>
<td>D1 (L, W, H: +3, -5 mm)</td>
</tr>
<tr>
<td>Shear strength</td>
<td>0,15 N/mm²</td>
</tr>
<tr>
<td>Reaction to fire</td>
<td>Euro class A1</td>
</tr>
<tr>
<td>Vapour permeability</td>
<td>µ = 5/15</td>
</tr>
<tr>
<td>Durability</td>
<td>complies</td>
</tr>
<tr>
<td>Toxic substances</td>
<td>none</td>
</tr>
</tbody>
</table>
Questions to be answered

Is it okay to use FeMo-slag, a waste product?
- Industrial by-product that can be used in construction applications
- Several regulations on secondary raw material

What are the risks?
- Chemical contaminations interacting with cement? Causing swelling & damage to the end-product? Causing visual damage?

Visual perception?

Influence on the weight?
- Ergonomics on construction site & cost of transportation
- Isolation properties? Weight reduction without loss of strength?
- Weight increase? Soundproofing?

Introduction | Production process | Materials | FeMo-slag | Mix design | Properties of ‘R-blocks’ | to the market | Conclusions
First test results of “FeMo-block”
- Solid block
- No weight loss
- FeMo-slag was visible at the outside
- FeMo-slag: looks like glass, different colours and shades of green and blue
- People will start asking questions

More intensive testing & communication to the public
- “FeMo-block” → ’Recy-block’ → ‘R-block’
Bringing ‘R-block’ to the market

- 2006/04/01: CE-labelling!
  - New European Standard EN 771 – 3
- Next step: BENOR → important for the Belgian Market
  - Chemical & mineralogical study: FeMo-slag acts as an inert material → aggregate for concrete
  - Physical study: NBN EN 993-1 → every 2000 tons
  - Influence on hydraulic reaction of cement?
  - Durability tests: frost & thaw, ASR → no risk
  - Environmental safety → VITO → leaching within limits
‘R-block’

- Reference = standard block
- R-block
- Cement
- Sand
- FeMo-slag
- Stone 2/6,3
Conclusions

- FeMo-slag
  - Can *successfully* be used to manufacture concrete blocks
  - All properties meet BENOR requirements
  - No hazard to human life or the environment

- ‘waste-to-product’ is not easy
  - Prejudice of “waste” → ‘industrial by-product’

- Marketing the product
  - CE-label, BENOR certificate,..., → “eco-label”
  - Open communication with client
  - Competitive price
Contact

KHBO – IW&T – Bouwkunde
Luc Boehme
Head of Department of Construction

Zeedijk 101
8400 Oostende

Tel (direct): 059/56 90 56
Fax (direct): 059/56 90 57
luc.boehme@khbo.be
luc.boehme@bwk.kuleuven.be
http://users.khbo.be/recyclage_kp