DTU Environment

Environmental screening of MSWI fly ash treatment technologies

Working Package 2 – Analysis of the technologies

Maresca Alberto, Thomas Fruergaard Astrup

November 2018

PREFACE

The report provides a preliminary assessment of the potential fate of selected elements of typical environmental concern associated with the treatment and management of municipal solid waste incineration (MSWI) fly ash in Denmark. None of the investigated technologies is currently operating at full scale in Denmark. At present, MSWI fly ash generated in Denmark is primarily sent abroad.

This study was conducted by DTU Environment in the period June - November 2018 and is part of work package n. 2 in the project "Future handling of fly ashes" (i.e. "Fremtidig håndtering af flyveaske"). The working group of work package n. 2 comprises DTU Environment and Rambøll A/S.

The report is confidential and only intended for internal decision support as part of a wider range of assessments aiming at investigating possible management options for MSWI fly ash in Denmark. It does not aim to support comparative assertions intended to be disclosed to the public.

The technologies selected to be investigated do not aim to cover the full list of technologies available on the market. The choice of technologies reflects the results of an earlier screening carried out by Rambøll A/S, aiming at clarifying potentially available fly ash treatment technologies based on their technical maturity, commercial maturity and material recovery.

The report was prepared by Alberto Maresca and Thomas Fruergaard Astrup from DTU Environment.

DTU, November 2018.

ABBREVIATIONS

100y:	100 years
500y:	500 years
C8-Aggr:	Carbon8 aggregates
MSWI:	Municipal Solid Waste Incineration

Contents

1. METHODOLOGY

The present section provides a detailed description of the applied methodology: the goal of the environmental screening, the functional unit and reference flow, the system boundaries, the scenarios, the data inventory, the material and substance flow analyses, the estimation of potential emissions to the environment and the substance concentration efficiency of the individual scenarios. The project group agreed on the scenario structures and main technologies, as well as the system boundaries.

1.1 GOAL AND SCOPE

Based on available data for selected fly ash treatment technologies, the purpose of this study is to evaluate and compare potential emissions and metal recoveries considering the time horizons of 100 years (100y) and 500 years (500y). For a range of selected scenarios, the purpose is further to quantify the "concentrating" and "dilution" potential of the technologies through a statistical entropy indicator. The investigated elements included As, Cu, Cr, Hg, Pb and Zn, representing metal(loid)s of typical concern with a relatively high impact to the environment (i.e. As, Cu, Cr, Hg, Pb and Zn) and targeted metals suitable for recovery (i.e. Zn, Pb and Cu).

Emissions of greenhouse gasses, energy consumptions and substitution of virgin materials are not part of this initial environmental screening assessment.

1.2 FUNCTIONAL UNIT AND REFERENCE FLOW

The functional unit is:

"The treatment of MSWI fly ash in Denmark, including the management of the generated residues and products."

The reference flow is:

"1 metric tonne of MSWI fly ash"

1.3 SYSTEM BOUNDARIES

The time horizons of the impacts in this environmental screening are 100y and 500y. The two time horizons may be considered to represent a "short-term" (100y) and a "long-term" (500y) perspective. As such, the chosen 100y and 500y are not meant to be too literally, but rather represent some rounded periods which coincide with what is typically used within Life Cycle Assessments. The geographical scope is Denmark and the temporal scope is 2020 – 2030.

The system boundaries include the treatment of MSWI fly ash, the cascade management of the individual technology outputs and the expected release of contaminants (i.e. As, Cu, Cr, Hg, Pb and Zn) from any of the generated residues and products. The study focuses only on the contaminants contained in the main waste flows entering the fly ash treatment facility, i.e. fly ashes, liquid residues from the acid scrubber and sulphuric acid residues; the potential presence of contaminants in auxiliary reagents is not accounted for. The emissions due to machinery operation (e.g. combustion of diesel), upstream processes (e.g. production of additives) and transportation processes are not considered.

1.4 SCENARIOS

Seven scenarios, i.e. one per each treatment technology, were considered – see Figures A0, A1, A2, A3, A4, A5 and A6 in Appendix A. The individual technology outputs were evaluated on a case-by-case basis to determine suitable cascade management options, which were then discussed within the working group and agreed upon. It is noteworthy, that the individual technologies have different commercial and technical maturity, which in turns affects the overall availability of data (e.g. limited information on the expected composition and mass flows of specific technology outputs), making the selection of cascade management processes possibly based on very limited information.

Scenarios S0a and S0b: reference scenario, i.e. current practice.

Currently, Danish MSWI fly ash is sent either to Norway or to Germany, where it is treated. These scenarios represent the reference scenarios, i.e. the current treatment and handling of fly ashes.

In the case of Norway, MSWI fly ashes are treated with the NOAH process at Langøya island (Scenario S0a – see Figure A0). This treatment consists of a neutralization process between liquid acid residues (i.e. mainly sulphuric acid residues from Kronos Titan AS, Fredrikstad, Norway), the alkaline MSWI fly ash and possibly other alkaline wastes (NGI, 2018). During the neutralization process, heavy metals (which represent a small percentage of the disposed material, i.e. up to 1-3%) are stabilised into new mineralogical forms with a relatively low water solubility or are bounded onto iron hydroxides (NGI, 2018). The end-product of the neutralization process is a gypsum slurry that consolidates over time under the weight of new gypsum slurry settling on top of the older one. The consolidation process induces the excess of pore water to be squeezed towards the less compacted layers, i.e. the top layers (geotechnical surveys on the consolidated gypsum slurry has described it as a standard consolidated silt (NGI, 2004)). The excess of pore water (i.e. wastewater) is treated onsite, and the treated wastewater is discharged into the surrounding marine environment. The overall pore water dynamics within the Langøya island limits (“inhibits”) the potential migration of wastewater through the surrounding low-permeable rocks.

In the case of Germany (Scenario S0b – see Figure A0), MSWI fly ashes are used as a backfilling material of salt mines; salt can be used to fill the gaps between the big bags filled with fly ash and to create a "flush connection" with the surrounding rock mass (K+S Entsorgung, 2018; Prognos AG et al., 2012). The surrounding salt rocks have a very limited permeability (i.e. $<10^{-16}$ m/s), which limits ("inhibits") the infiltration of water into the salt mine (Prognos AG et al., 2012).

Scenario S1: landfill without pre-treatment

The direct landfilling of MSWI fly ash without any pre-treatment is included as a useful reference for discussion of the results (see Figure A1), irrespective of whether this may be considered a realistic option for the future management of these residues in Denmark.

Scenario S2: Carbon8

MSWI fly ash is treated in the technology Carbon8 in order to make the so-called Carbon8 aggregates (C8-Aggr), which is the only output generated from the Carbon8 technology. Scenario S2 is represented in Figure A2.

C8-Aggr can be used by concrete manufactures during the production of concrete blocks, which can be utilised in a variety of building applications ("primary use"; e.g. during the construction of internal and external walls). Maintenance/demolition activities can then crush these blocks and recycle them into new construction works, where the C8-Aggr are still encapsulated into some kind of concrete product (e.g. another concrete block): the newly generated concrete aggregates originating from crushing operations can be assumed to replace part of the gravel used during concrete manufacturing. In principle, multiple demolitions and manufacturing cycles can potentially occur, affecting the overall duration of this "primary use" phase. For simplicity, it was assumed that the "primary use" phase has a duration of 100y.

At the end of their "primary use" phase, the concrete products are crushed during new maintenance/demolition activities and the newly generated concrete aggregates can be used in loose aggregate applications ("secondary use"), for example as an aggregate material during the construction of road sub-bases substituting other virgin materials (e.g. gravel). Again, loose aggregates may be removed and used somewhere else, but still within loose aggregate applications with low grade uses (see Purnell and Dunster (2009) for an overview of the potential applications of crushed concrete). For simplicity, it was assumed that the "secondary use" phase has a duration of 100y.

At the end of their "secondary use" phase, it was assumed that the concrete aggregates are sent to a final placement (e.g. a landfill for inert waste).

Scenarios S3 and S3+Cu: FLUREC

MSWI fly ash is treated in the technology FLUREC. The main outputs of this technology are treated fly ashes, a "resin + Hg" flow (Hg is bound to a selective resin with high affinity for Hg), a bottom ash flow (originating from the recirculation of the washed filter cake and the gypsum slurry back to the furnace), a metallic cementate flow enriched in Pb, a flow enriched with metallic Zn and wastewater.

The flows enriched in Pb and Zn are assumed to be sent to smelters, with landfilling of the smelter residues. Bottom ashes are assumed to be used as an aggregate material during the construction of road sub-bases, similarly to current Danish practice. Loose aggregates may be removed over time and used in other road sub-bases and/or embankment applications; for simplicity, it was assumed that after 100y of road lifetime, the bottom ashes are landfilled. The treated fly ash and the "resin + Hg" flow are landfilled. Wastewater is assumed to be treated onsite before discharge; the generated sludge is landfilled (in Figure A3 the sludge flow has been combined with the treated fly ash flow).

An additional scenario with the possibility of Cu recovery from the Pb-smelter residues was considered, i.e. Scenario S3+Cu (see Figure A3). The scenario without Cu recovery is referred to as Scenario S3, where the Pb-smelter residues are assumed to be landfilled without any further treatment.

Scenario S4: FLUWA

MSWI fly ash is treated in the technology FLUWA. The main outputs of this technology are treated fly ashes, a "resin + Hg" flow (Hg is bounded to a selective resin with high affinity for Hg), a bottom ash flow (originating from the recirculation of the washed filter cake and the gypsum slurry back to the furnace), a metallic cementate flow enriched in Zn and Pb and wastewater. Scenario S4 is represented in Figure A4.

The metallic cementate is assumed to be sent to a Zn smelter, which residues are sent to a Pb smelter. The residues from the Pb smelter are landfilled. The treated fly ashes and the "resin + Hg" flow are landfilled. Wastewater is assumed to be treated onsite before discharge; the generated sludge is landfilled.

Scenario S5: Halosep

MSWI fly ash is treated in the technology Halosep. The main outputs of this technology are treated fly ashes, a sludge enriched in heavy metals, bottom ashes (originating from the recirculation of the "oversize fraction" (>1 mm) flow back to the furnace) and salt brine. Scenario S5 is represented in Figure A5.

The sludge enriched in heavy metals is assumed to be sent to a Zn smelter, which residues are sent to a Pb smelter. The residues from the Pb smelter are landfilled. Bottom ashes are assumed to be used as an aggregate material during the construction of road sub-bases, similarly to current Danish practice. Loose aggregates may be removed over time and used in other road sub-bases and/or embankment applications; for simplicity, it was

assumed that after 100y of road lifetime, the bottom ashes are landfilled. The treated fly ash is landfilled. The salt brine is assumed to be discharged into a marine environment, without any further treatment.

Scenario S6: Renova

MSWI fly ash is treated in the technology Renova. The main outputs of this technology are treated fly ashes, a "resin + Hg" flow (Hg is bounded to a selective resin with high affinity for Hg), a bottom ash flow (originating from the recirculation of some of the treated fly ashes back to the furnace), a flow enriched with metallic Zn, wastewater and evaporated water. Scenario S6 is represented in Figure A6.

The flow enriched in Zn is assumed to be sent to smelters, with landfilling of the smelter residues. Bottom ashes are assumed to be used as an aggregate material during the construction of road sub-bases, similarly to current Danish practice. Loose aggregates may be removed over time and used in other road sub-bases and/or embankment applications; for simplicity, it was assumed that after 100y of road lifetime, the bottom ashes are landfilled. The treated fly ash and the "resin + Hg" flows are landfilled. Wastewater is assumed to be treated onsite before discharge; the generated sludge is landfilled.

1.5 TECHNOLOGY DATA

In order to allow direct comparison across different technologies, the selected composition of MSWI fly ash and liquid residues from the acid scrubber were identical in all scenarios. "Typical compositions" were estimated by Rambøll A/S, using a weighted average across a range of observations. In order to account for expected variations in composition in the MSWI fly ash and the liquid residues from the acid scrubber, the "typical compositions" were assumed to be normally distributed: the mean value was assumed equal to the weighted averages and the standard deviation was assumed equal to the minimum distance between the highest observation point from the weighted average and the lowest observation point from the weighted average (i.e. a sort of a weighted standard deviation). Table 1 reports the compositions of the MSWI fly ash and the liquid residues from the acid scrubber.

The composition of the sulphuric acid residue used in Scenario S0a (NOAH treatment) was assumed identical to the composition reported in NGI (2018), which are based on five observations during the period 2016-2017. The composition of the sulphuric acid residue is presented in Table 1.

An analysis of the expected (approximate) composition of the individual flows entering and exiting the individual technologies was carried out by Rambøll A/S. DTU Environment and Rambøll A/S worked together in order to generate a consistent material and substance flow analysis across the individual technologies. Transfer coefficients referring to the amounts of materials and substances transferred in each of the technology outputs were recalculated and used to represent the expected operating conditions of the technology.

Metal smelters were assumed to be 100% efficient with respect to the recovery of the desired metals, i.e. no residual amounts of the desired metal in the smelter residues and no impurities in the desired flow. This assumption implies that the calculated amounts of recovered metals should be understood as potentials.

Table 1. Compositions of the MSWI fly ash, the liquid residues from the acid scrubber and the sulphuric acid residues.

	MSWI fly ash composition:			Liquid residues from acid scrubber			Sulphuric acid residues		
	Weighted average mg/kg		2xStand.Dev. mg/kg	Weighted average mg/kg		2xStand.Dev. mg/kg	Weighted average mg/kg		2xStand.Dev. mg/kg
Ag	20	±	10						
Al	26000	±	17000	2	±	1	287	±	16
As	280	±	230				0.08	±	0.02
Ba	1300	±	400	400	±	400	0.07	±	0.04
Bi	90	±							
Ca	145000	±	59000	1380	±	1360			
Cd	250	±	210	0.3	±	0.3	0.02	±	0.01
Cl	67000	±	27000	50000	±	10000			
Co	20	±					15	±	2
Cr	510	±	300	0.1	±	0.1	231	±	12
Cu	2300	±	1400	2	±	1	1.8	±	0.2
F	1400	±	300						
Fe	11000	±	1000	10	±	10	32758	±	13751
Hg	3	±	2	1.5	±	0.5	0.000020	±	0.000002
K	50000	±	34000	120	±	70			
Li	4600	±	4500	5	±	5			
Mg	12000	±	5000	250	±	140			
Mn	700	±	700	30	±	n.a.	616	±	34
Mo	20	±	10				0.34	±	0.11
Na	51000	±	27000	300	±	140			
Ni	70	±	30				22.3	±	2.3
P	6000	±	1000	9	±	8			
Pb	6000	±	5000	9	±	2	1.18	±	0.37
Rb	160	±	10						
S	50000	±	29000	270	±	60	95385	±	9539
Sb	1000	±	600	0.5	±	0.5	3.1	±	1.0
Sc	2	±							
Se	30	±							
Si	60000	±	19000	50	±	10			
Sn	1300	±	500	1	±	n.a.	0.21	±	0.07
Sr	400	±	300	30	±	20			
Ti	8000	±	1000	1	±	n.a.	2678	±	404
TOC	9000	±							
V	50	±	20				444	±	24
W	90	±							
Y	10	±							
Zn	25000	±	14000	50	±	20	21	±	8
Zr	70	±	10						

1.6 EMISSIONS TO THE ENVIRONMENT

If not recovered, substances can be either emitted to the environment or "stored" within the technosphere (e.g. in a landfill). The partitioning of a specific substance between emissions to the environment or "stored emissions" depends, among other factors, on the considered time horizon; landfills, for example, can have a very slow release to the environment and may therefore be considered as "long-term stocks".

Releases to the environment were estimated based on literature data and expected L/S ratios calculated based on Danish conditions. The landfill leachate was assumed to be actively collected and treated during the early operation of the landfill; the active collection of leachate was assumed to have an overall efficiency of 80% over the initial 100y, meaning that the remaining 20% was assumed to be emitted to the environment. After 100y, 100% of the generated leachate was assumed to be emitted to the environment.

The leaching from MSWI bottom ashes used as an aggregate material for the construction of road sub-bases was estimated based on column leaching tests carried out with Danish MSWI bottom ashes (Astrup et al., 2009). The expected L/S ratio which the bottom ashes would be in contact with during the assumed 100y of lifetime of the road sub-base layer was calculated similarly to Allegrini et al. (2015). The expected L/S ratio based on Allegrini et al. (2015) is a log normal distribution skewed to the left with a median value of 4.9 L/kg. The expected leaching from bottom ashes at L/S 4.9 L/kg was based on data from Allegrini et al. (2015), who extrapolated the column leaching results from Astrup et al. (2009) at specific L/S ratios. After road maintenance /demolition (i.e. after the first 100y), bottom ashes are assumed to be landfilled for another 400 years. The cumulative release over these 400 years of landfill was extrapolated from Allegrini et al. (2015) figures, considering a cumulative L/S ratio in the landfill of approximately 10 L/kg – see next paragraph.

The leaching from treated MSWI fly ash was estimated based on column leaching tests carried out for untreated MSWI fly ashes from Hyks et al. (2009), Quina et al. (2011) and Zhang et al. (2016). The expected L/S ratio which the landfilled (treated fly) ashes will be in contact with during the assumed time horizons (T) of 100y and 500y were calculated similarly to the approach proposed by Kosson et al. (1996):

$$L/S\ [L\ \cdot kg^{-1}] = \frac{I\ [\%] \cdot T[years]\ \cdot P[mm \cdot year^{-1}]}{\rho[kg \cdot m^3] \cdot h[m]}$$

Annual Danish precipitation (P) was assumed to be normally distributed, i.e. 790 ± 50 mm^{-1} $year^{-1}$ (assumption based on Danish precipitation data, i.e. DMI (2017)); infiltration rates (I) through the landfill were based on Di Gianfilippo et al. (2016) model calculations, i.e. ~22% infiltration rate (± an assumed 5% variation), and considering that the landfill is uncovered during the first two years of operation (assumed infiltration of 500 mm over the two years); the bulk density (ρ) of MSWI fly ash density was assumed to be uniformly distributed between 660 kg/m^3 (Quina et al., 2008) and 1010 kg/m^3 (Polettini et al., 2004); the height of the landfill (h) was assumed to be 10 m. The expected L/S ratios at 100y and 500y were calculated at 2.1 and 10.5 L/kg, respectively,

and it was considered appropriate to use the available literature data at L/S 2.0 and 10 L/kg (Hyks et al., 2009; Quina et al., 2011; Zhang et al., 2016). Transfer coefficients were calculated from the individual column experiments by dividing the analytical released amounts by the total ash contents.

The release of individual substances from treated MSWI fly ash was assumed to follow the same transfer coefficients calculated for untreated MSWI fly ash. The same transfer coefficients were also used in the case of landfills for smelter residues and wastewater sludge. The landfilling of "resin+Hg" and "TMT+Hg" was assumed to have no leaching of Hg, as Hg is generally among the elements presenting the highest complexation affinity with the resins/TMT, thereby limiting the subsequent release.

The fly ash treatment technologies from scenario S3 (Flurec), S4 (Fluwa) and S6 (Renova) included the generation of wastewater, which was assumed to be treated onsite (by local wastewater treatment plants) and then discharged. The discharged water was assumed to have a composition equal to half of the permitted limit values. In Scenario S0a (NOAH treatment), the excess of pore water was assumed to be pumped out, treated and eventually discharged to the surrounding marine environment: the composition of the discharged water was assumed to be equal to half of the permitted limit values (Miljø-Direktoratet, 2014; NGI, 2004).

The leaching from concrete products made with C8-Aggr was estimated based on the environmental product declaration of C8-Aggr (Carbon8, 2011), which defines the maximum leachable amounts of specific substances based on the EN 12457-4:2002 standard (i.e. one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 10 mm, without or with size reduction). It was assumed that: i) during their "primary use" (i.e. when encapsulated into a concrete matrix; 100y), the concrete blocks could leach up to one-tenth of the maximum allowed criteria defined for C8-Aggr; ii) during their "secondary use" (i.e. when the crushed concrete is used as a loose aggregate during the construction of road sub-bases; 100y), the demolished concrete blocks would leach the remaining allowable releases defined for C8-Aggr, i.e. the remaining nine-tenth; iii) during their final placement in a landfill for inert waste (300 years), the demolished concrete blocks were assumed to release up to the limit values defined for waste acceptable at landfills for inert waste at the L/S ratio 10 L/kg (Directive 2003/33/EC, 2003).

The hydraulic conditions of the two reference scenarios "inhibits" the potential migration of contaminants through leaching from the disposed residues to the surrounding environment (see description of these scenarios in Section 1.4). Accordingly, potential direct emissions to the environment due to leaching were assumed equal to zero.

1.7 MATERIAL FLOW ANALYSIS AND STATISTICAL ENTROPY

Material Flow Analysis and Substance Flow Analysis calculations were carried out using the freeware STAN v.2.6.801 (http://www.stan2web.net/). The software accepts normally distributed data as input for mass and substance flows, and allows data reconciliation and error propagation.

The uncertainty related to the composition of the input flows and to the transfer coefficients used in the individual processes (e.g. leaching release from the bottom ashes used in road construction) was propagated into the model, resulting into normally distributed compositions of the output flows.

Depending on the specific treatment process, different output flows are generated by the individual treatment technologies. Specific substances can be extracted and enriched in some of the flows, whereas others may be diluted, for example by using the MSWI fly ash as a secondary material during the manufacture of concrete. Statistical entropy calculations were used as an indicator to describe the overall substance dilution or concentration owing to the individual management scenarios. As an example, the direct use of fly ashes in concrete manufacture results in negative concentration efficiencies for any chosen substance, because the fly ash mass is diluted by the total mass of the concrete product. While a full explanation of the methodology can be found in Laner et al. (2017) and Rechberger (2001), a positive substance concentrating efficiency indicates that the substance mass has been concentrated on fewer flows or in higher concentrations (e.g. in the case of extraction and recovery of Zn), while negative values indicate that the substance has been diluted or distributed over more flows (e.g. the use of fly ashes in concrete manufacture).

2. RESULTS

2.1 EMISSIONS AND METAL RECOVERY

Figure 1 shows the amounts of As, Cr, Cu, Hg, Pb and Zn entering the individual technologies, per tonne of fly ash being treated, while Appendix B reports the Substance Flow Analyses figures for the individual scenarios at the time horizon 500y. Figure 1 shows that comparable amounts of As, Cr, Cu, Pb and Zn entered the individual technologies. This is because the main source of these elements was the MSWI fly ash flow, irrespective of whether the liquid residues from the acid scrubber or the sulphuric acid residues were used by the treatment technology (the slightly higher amounts of Zn entering Scenario S3 are primarily due to the additional use of Zn powder as input to the Flurec technology). It is noteworthy, however, that slightly higher levels of Cr were observed in the case of Scenario S0a, as an effect of the relatively high concentration (and amounts) of Cr in the sulphuric acid residues (230 ± 10 mg/kg).

Differently than for As, Cr, Cu, Pb and Zn, the amounts of Hg entering the individual scenarios are affected by the amounts of liquid residues from the acid scrubber being used by the fly ash treatment technology, and this is because of the relatively high concentration of Hg in these liquid residues (1.5 ± 0.5 mg/kg) and the relatively large volumes of liquid residues being used (in the range of 1400-3400 kg per tonne of fly ash, depending on the specific technology, i.e. the higher the Hg amounts entering the technologies, the larger volumes of liquid residues were used).

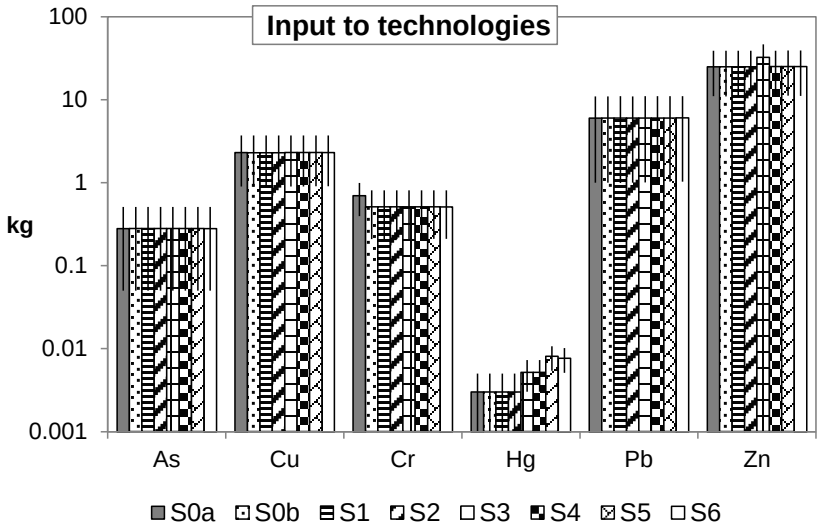


Figure 1. Amounts of As, Cr, Cu, Hg, Pb and Zn entering the individual technologies, per tonne of fly ash being treated. Error bars indicate the standard deviation associated with the composition of the input flows.

In terms of metal recovery, the potential recovery of Zn (calculated as the ratio between the fraction being recovered and the input amounts) from Scenarios S3-6 was relatively high: 84% for Scenario S5 (Halosep), ~71% for Scenarios S3 and S4 (Fluwa and Flurec) and 46% for Scenario S6 (Renova). The potential recovery of Pb was ~53% for Scenarios S3-4 (Fluwa and Flurec) and 32% for Scenario S5 (Halosep). Scenario S6 (Renova) did not include any Pb smelter, as the Zn smelter residues contained only ~1.6% of the total Pb in input to the Renova technology (the calculated concentration of Pb in these smelter residues was ~8 g/kg). The potential recovery of Cu from Scenario S3+Cu was ~24% (i.e. circa 0.55 kg of Cu per tonne of MSWI fly ash), suggesting that it can be worthwhile to include this process in Scenario S3 (Flurec).

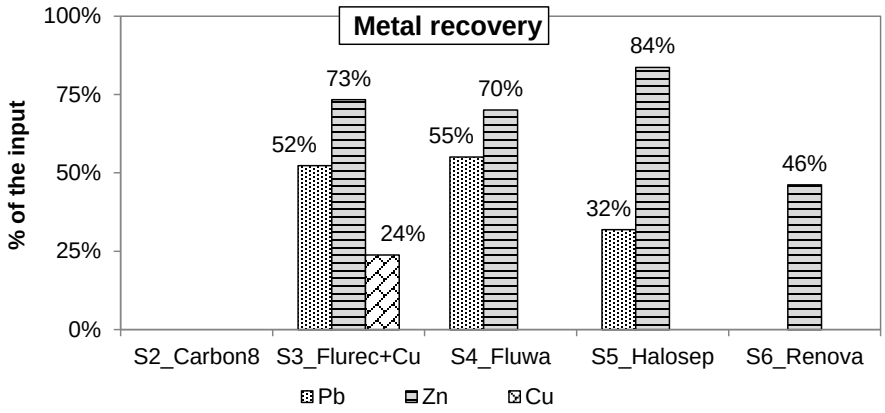


Figure 2. Potential metal recovery of Cu, Pb and Zn, expressed as potentially recoverable amounts and input.

Figure 3 shows the calculated emissions to the environment due to leaching across the individual scenarios, considering a time horizon of 100y and 500y. Noteworthy that these emissions were a few orders of magnitude lower than the technology inputs and the potentially recoverable amounts, indicating that large amounts of As, Cr, Cu, Hg, Pb and Zn are expected to remain stored within the technosphere (e.g. within a landfill) even at 500y – see the Substance Flow Analyses figures in Appendix B that show the calculated amounts of substances being recovered, emitted or stocked within the technophere per each of the scenarios.

In general, the cumulative release of all investigated elements increased with the considered time horizon, except for Scenario S0b (backfilling material of salt mines) for which no direct emissions were assumed. In the case of Scenarios S3-6, the cumulative releases at 500y were observed between 1.1 and 7.5 times higher than at 100y. For comparison, the observed increase in cumulative emissions for Scenario S2 (Carbon8) was higher: ~13 times higher for Cr, ~20 times higher for As, Hg, Pb and Zn, and ~140 times higher for Cu. The higher increase in cumulative emissions for Scenario S2 (Carbon8) compared with the other scenarios strongly depends on the assumptions made for Scenario S2 (i.e. the cumulative releases at 200 years were assumed to be equal to the maximum leachable criteria, based on the environmental product declaration; the following releases from the

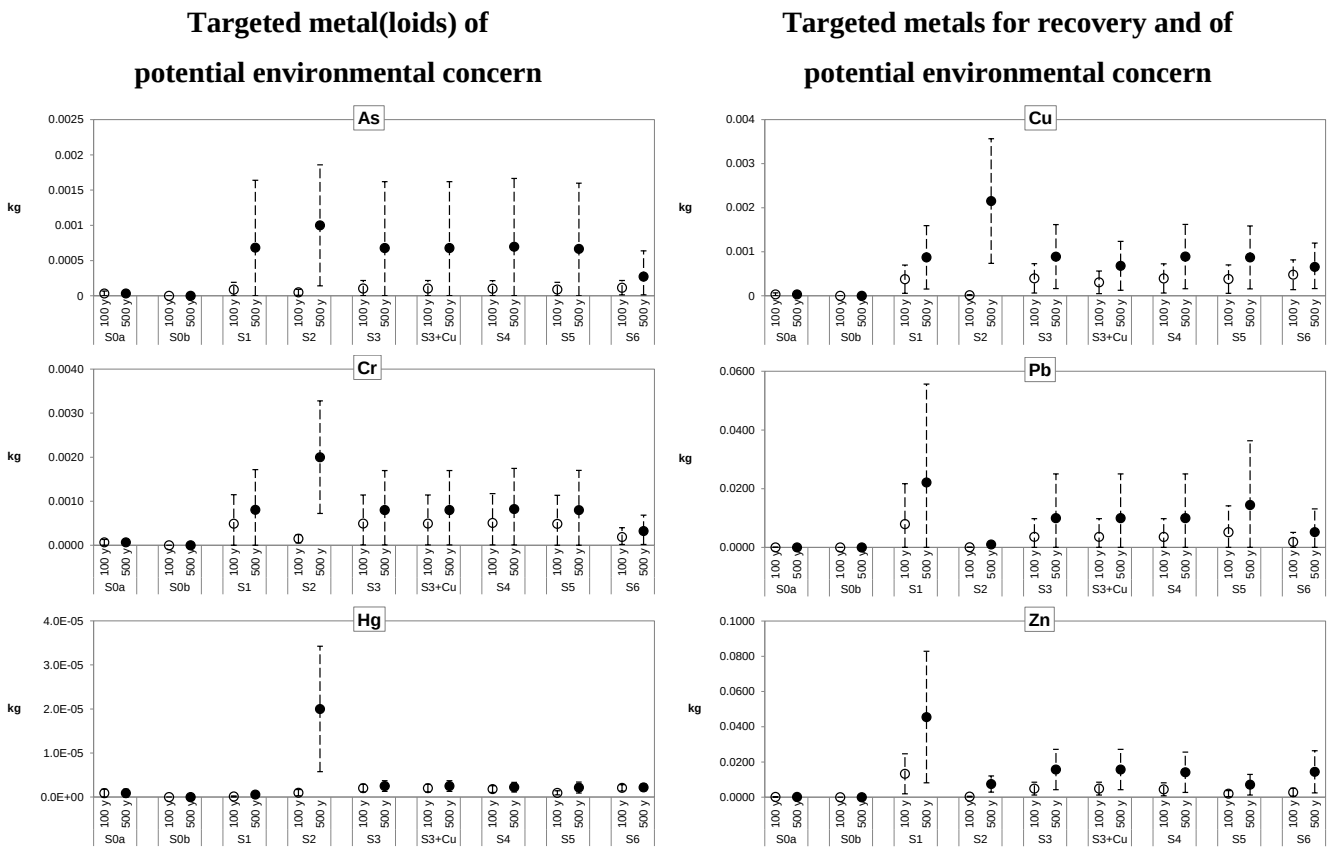


Figure 3. Amounts of As, Cr, Cu, Hg, Pb and Zn calculated to be released from the individual scenarios, considering a time horizon of 100y (○) and 500y (●). Dashed lines represent the standard deviation around the mean values. Note that the scale of the individual figures varies.

landfill were assumed to be equal to the limit values for waste acceptable at landfills for inert waste, which were often similar to the environmental product declaration of C8-Aggr, i.e. similar to the assumed cumulative releases at 200 years); on the other hand, poor information is available on the leaching behaviour of C8-Aggr, under for example short-/long- term leaching or different pH conditions, which makes it difficult to estimate potential emissions to the environment.

In terms of expected emissions to the environment, Scenarios S3-6 (Flurec, Fluwa, Halosep and Renova) showed rather similar environmental performances both at 100y and 500y, i.e. variations in expected emissions to the environment were generally observed within a factor of two. A more detailed look at these technologies revealed that Scenario S6 (Renova) performed slightly better in terms of As, Cr, Cu and Pb emissions, and that Scenario S5 (Halosep) released the lowest amounts of Zn. Scenario S2 (Carbon8) showed lower emissions to the environment than Scenarios S3-6 during the first 100y for all considered elements, but at 500y the situation was

generally reversed. Scenario S1 (landfill without pre-treatment) demonstrated emissions to the environment comparable to Scenarios S3-6 for As, Cu, Cr and Hg, whereas the emissions of Pb and Zn were found to be slightly higher.

In general, the potential variability in composition of the input flows resulted into considerable variations in the calculated amounts of potentially recoverable metals, stored substances and emissions to the environment – see error bars in Figure 3. In particular, the results from Figure 2 indicate that changes in MSWI fly ash composition in one of the scenarios can affect its overall environmental performance compared to the other scenarios.

2.2 STATISTICAL ENTROPY: CONCENTRATIONS OR DILUTIONS

Table 2 reports the results of statistical entropy calculations for both time horizon 100y and 500y. Substance concentration efficiencies with values in the range of ± 5% represent cases for which the dilution/concentration of the individual element was not affected by the different scenarios in a considerable manner, and they are therefore not discussed here. Table 2 shows that the calculated substance concentration efficiencies at 100y and 500y were (practically) the same. This is because, even if the time horizon increases, there are no processes in the considered scenarios that tend to actively concentrate and/or dilute any of the given flows after 100y; the considered emissions to the environment due to leaching were not sufficiently large to affect the statistical entropy calculations to any significant extent.

The substance concentration efficiencies of Scenario S0b and S1 were equal to zero irrespective of the element considered. Although salt can be used in Scenario S0b (backfilling material of salt mines) to fill the gaps between the big bags filled with MSWI fly ash, this salt is not mixed with the fly ash itself; accordingly, no direct dilution of the ashes with the added salts was considered. With regards to Scenario S1, substance concentration efficiencies were practically zero, too – except for the relatively small and slow contribution of the emissions to environment, in which small fractions of the considered elements were able to exit the landfill together with the percolating leachate.

Substance concentration efficiencies were negative in both Scenarios S0a (NOAH treatment) and S2 (Carbon8) for nearly all the investigated elements. In the case of Scenario S2, MSWI fly ash material is mixed with other reactants/materials in order to make concrete blocks that have a total mass higher than the untreated fly ash, which in turn dilutes the composition of fly ashes over a larger mass (under the assumption that the other reactants/materials are “cleaner” that the fly ash itself). Similarly, in the case of Scenario S0a, the newly generated gypsum was estimated to have an overall mass larger than the input fly ash, resulting into a dilution of As, Cu, Hg, Pb and Zn. To the contrary, positive substance concentration efficiencies were calculated for Cr in Scenario S0a: the relatively large amounts of Cr transferred from the sulphuric acid residues (see Section 2.1) to the newly

generated gypsum residue summed with the amounts of Cr belonging to the ashes resulted into a final gypsum product that demonstrated a Cr concentration higher than the input waste flows. This effect was not observed in the case of As, Cu, Hg, Pb and Zn, because of their relatively low concentration in the sulphuric acid residues.

Pilot and full-scale applications of the herein investigated fly ash treatment technologies have been shown that valuable elements can be extracted from MSWI fly ash, making the latter a potentially valuable resource. As indicated by Laner et al. (2017), an efficient use of resources aims at minimising the dilution of substances during its use. Even though Scenarios S0a and S2 (NOAH treatment and Carbon8) use MSWI fly ashes for construction applications, they tend to dilute the ash composition, including the potentially valuable metals contained in these materials.

The substance concentration efficiencies of Pb, Zn and Cu were positive in all the scenarios that included the extraction and recovery of these metals. Positive substance concentration efficiencies were also showed for Hg in all the scenarios that included extraction and recovery of metals: this is because during the process of extracting the desirable metals, a considerable fraction of Hg can also be extracted; this extracted Hg is irreversibly fixed to various kinds of selective resins, and exits the individual MSWI fly ash treatment technology in a relatively concentrated flow (e.g. “resin + Hg”).

Table 2: Statistical entropy results for the individual scenarios at the time horizons 100y and 500y. Red cells highlight substance concentration efficiencies below -5%, i.e. dilutions, whereas the green cells highlight substance concentration efficiencies above +5%, i.e. concentrations.

Substance Concentrating Efficiency at 100 years						
	As	Cr	Cu	Hg	Pb	Zn
S0a (NOAH process)	-3%	4%	-4%	-2.0%	-5%	-7%
S0b (Backfilling in salt mines)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
S1 (Landfill without pre-treat.)	0.0%	-0.1%	0.0%	0.0%	-0.2%	-0.1%
S2 (Carbon8)	-35%	-38%	-47%	-23%	-56%	-78%
S3 (Flurec)	-3.5%	-3.8%	13%	23%	43%	55%
S3+Cu (Flurec+Cu recovery)	-3.5%	-3.8%	17%	23%	43%	56%
S4 (Fluwa)	-3.0%	-3.3%	-1.9%	23%	46%	59%
S5 (Halosep)	2.3%	-3.9%	0.3%	8.9%	24%	75%
S6 (Renova)	1.6%	2.3%	2.5%	49%	3.3%	39%
Substance Concentrating Efficiency at 500 years						
	As	Cr	Cu	Hg	Pb	Zn
S0a (NOAH process)	-3%	4%	-4%	-2.0%	-5%	-7%
S0b (Backfilling in salt mines)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
S1 (Landfill without pre-treat.)	-0.3%	-0.2%	-0.1%	0.0%	-0.6%	-0.5%
S2 (Carbon8)	-35%	-38%	-47%	-23%	-56%	-78%
S3 (Flurec)	-3.7%	-3.9%	13%	23%	43%	55%
S3+Cu (Flurec+Cu recovery)	-3.7%	-3.9%	17%	23%	43%	56%
S4 (Fluwa)	-3.2%	-3.3%	-1.9%	23%	46%	58%
S5 (Halosep)	2.1%	-4.0%	0.2%	8.9%	23%	75%
S6 (Renova)	1.5%	2.3%	2.5%	49%	3.2%	39%

3. CONCLUSIONS

The purpose of this study was to evaluate and compare potential emissions and metal recovery considering time horizons of 100 years (100y) and 500 years (500y) for a selected number of elements, and to quantify the "concentrating" and "dilution" potential of the technologies through a statistical entropy indicator. Emissions of greenhouse gasses, energy consumptions and substitution of virgin materials were not part of this initial environmental screening assessment.

Relatively high potential recovery of Zn were observed for all fly ash treatment technologies with Zn extraction, especially Halosep (84% of the total entering Zn), Flurec (73%) and Fluwa (70%). The potential recovery of Pb was lower than Zn, but still considerable: the highest Pb recovery was calculated for Fluwa (55%), followed by Flurec (52%) and Halosep (32%). A potential for Cu recovery was observed in the case of Flurec (24%), where a considerable amount of Cu was routed to the cementate flow. It is noteworthy that the calculated recovery rates are based on estimates representing the expected operating performance of the individual technologies, and should therefore be understood as estimations. Overall, however, the Flurec process demonstrated relatively high recovery rates for all Zn, Pb and Cu.

Based on a 500y time horizon, Scenario S2 (Carbon8) demonstrated higher emissions to the environment than all other fly ash treatment technologies, i.e. Scenarios S3-6. It is noteworthy, however, that very limited data on the potential leaching behaviour of Carbon8 products was available, and that the calculated emissions from this scenario were strongly dependent on the scenario assumptions. Comparable emissions to the environment were estimated in the case of Scenarios S3-6 (Flurec, Fluwa, Halosep and Renova), although Scenario S6 (Renova) performed slightly better in almost all cases.

Negative substance concentration efficiencies were calculated in the case of Scenario S2 (Carbon8). While this scenario uses fly ash in combination with other reagents/materials in order to make products suitable for construction purposes, the potentially valuable substances contained in the ashes are diluted, making the potential future access to these substances more difficult. Furthermore, in contrast to the other technologies, the fate of the demolished concrete blocks containing Carbon8 is unclear, as they could be distributed potentially anywhere in the society.

Last but not least, it should be noted that the individual technologies were investigated assuming a standard composition of the input fly ash and liquid residues from the acid scrubber, using fixed treatment efficiencies and disregarding the fact that specific technologies may be more suitable than others depending on the specific waste-to-energy plant conditions, e.g. type of flue gas cleaning system, or fly ash characteristics. These factors are able

to affect the overall performance of the individual technologies (and corresponding scenarios), as for example in terms of recoverable amounts of metals and emissions to the environment.

4. REFERENCES

Allegrini, E., Butera, S., Kosson, D.S., van Zomeren, A., van der Sloot, H., Astrup, T.F., 2015. Life cycle assessment and residue leaching: The importance of parameter, scenario and leaching data selection. Waste Manag. 38, 474–485. doi:10.1016/j.wasman.2014.12.018

Astrup, T.F., Pedersen, A.J., Hyks, J., Frandsen, F.J., 2009. Residues from waste incineration. Final report PSO-5784. Department of Environmental Engineering, Technical University of Denmark (DTU), Kgs. Lyngby.

Carbon8, 2011. Carbon8 Aggregates Ltd standard for “Block Aggregate” Specification.

Di Gianfilippo, M., Costa, G., Pantini, S., Allegrini, E., Lombardi, F., Astrup, T.F., 2016. LCA of management strategies for RDF incineration and gasification bottom ash based on experimental leaching data. Waste Manag. 47, 285–298. doi:10.1016/j.wasman.2015.05.032

Directive 2003/33/EC, 2003. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to article 16 of and Annex II to Directive 1999/31/EC.

DMI, 2017. Klimadata Danmark ver. 4 (inkl. landstal). Kommunale og landets referenceværdier 2006-2015. Måneds- og årsværdier for temperatur, nedbør og solskin. Kommunernes og landets generelle vejr og klima. Klimadata anvendt i ”Trap Danmark 6. udgave”. DMI rapport.

EN 12457-4:2002, 2002. Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 4: One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 10 mm (without or with size reduction).

Hyks, J., Astrup, T., Christensen, T.H., 2009. Long-term leaching from MSWI air-pollution-control residues: Leaching characterization and modeling. J. Hazard. Mater. 162, 80–91. doi:10.1016/j.jhazmat.2008.05.011

K+S Entsorgung, 2018. Underground Recovery, Stacking Backfill [WWW Document]. URL http://www.ks-entsorgung.com/en/geschaeftsfelder/verwertung/index.html (accessed 10.31.18).

Kosson, D.S., van der Sloot, H., Eighmy, T.T., 1996. An approach for estimation of contaminant release during utilization and disposal of municipal solid waste combustion residues. J. Hazard. Mater. 47, 43–75. doi:10.1016/0304-3894(95)00109-3

Laner, D., Zoboli, O., Rechberger, H., 2017. Statistical entropy analysis to evaluate resource efficiency: Phosphorus use in Austria. Ecol. Indic. 83, 232–242. doi:10.1016/j.ecolind.2017.07.060

Miljø-Direktoratet, 2014. Oversendelse av en rett tillatelse - NOAH Langøya.

NGI, 2018. Deponi for nøytralisert og stabilisert uorganisk farlig avfall i Dalen gruve , Brevik.

NGI, 2004. NOAH - Langøya Miljørisikovurdering av deponiene på Langøya.

Polettini, A., Pomi, R., Trinci, L., Muntoni, A., Lo Mastro, S., 2004. Engineering and environmental properties of thermally treated mixtures containing MSWI fly ash and low-cost additives. Chemosphere 56, 901–910. doi:10.1016/j.chemosphere.2004.05.004

Prognos AG, RSP Riemann Sonnenschein & Partner GmbH, Jochen Schulte, 2012. Outlook for underground waste management in Germany. Verband der Kali- und Salzindustrie e. V. (VKS), Verband Bergbau, Geologie und Umwelt e. V. (VBGU).

Purnell, P., Dunster, A., 2009. 20. Recycling of concrete, in: Management, Recycling and Reuse of Waste Composites. pp. 569–591. doi:10.1533/9781845697662.5.569

Quina, M.J., Bordado, J.C.M., Quinta-Ferreira, R.M., 2011. Percolation and batch leaching tests to assess release of inorganic pollutants from municipal solid waste incinerator residues. Waste Manag. 31, 236–245. doi:10.1016/j.wasman.2010.10.015

Quina, M.J., Santos, R.C., Bordado, J.C., Quinta-Ferreira, R.M., 2008. Characterization of air pollution control residues produced in a municipal solid waste incinerator in Portugal. J. Hazard. Mater. 152, 853–869. doi:10.1016/j.jhazmat.2007.07.055

Rechberger, H., 2001. An entropy based method to evaluate hazardous inorganic substance balances of waste treatment systems. Waste Manag. Res. 19, 186–192. doi:10.1177/0734242X0101900210

Zhang, Y., Soleimanbeigi, A., Likos, W.J., Edil, T.B., 2016. Geotechnical and Leaching Properties of Municipal Solid Waste Incineration Fly Ash for Use as Embankment Fill Material. Transp. Res. Rec. J. Transp. Res. Board 2579, 70–78. doi:10.3141/2579-08

APPENDIX A. Material Flow Analyses of the individual scenarios

The following figures represent the calculated material flow analyses for the individual scenarios, as described in Section 1.4, for the time horizon 100y and 500y. The dashed lines represent the scenarios' system boundaries. Brown flows represent emissions to the environment; green flows represent recovered metals; orange flows and orange processes represent system stocks; light blue flows are model artefacts representing moisture contents and they are used within the systems to facilitate the tracking of dry solids when convenient for the calculations.

Commonly used abbreviations: FA: fly ash; BA: bottom ash; H2O: water

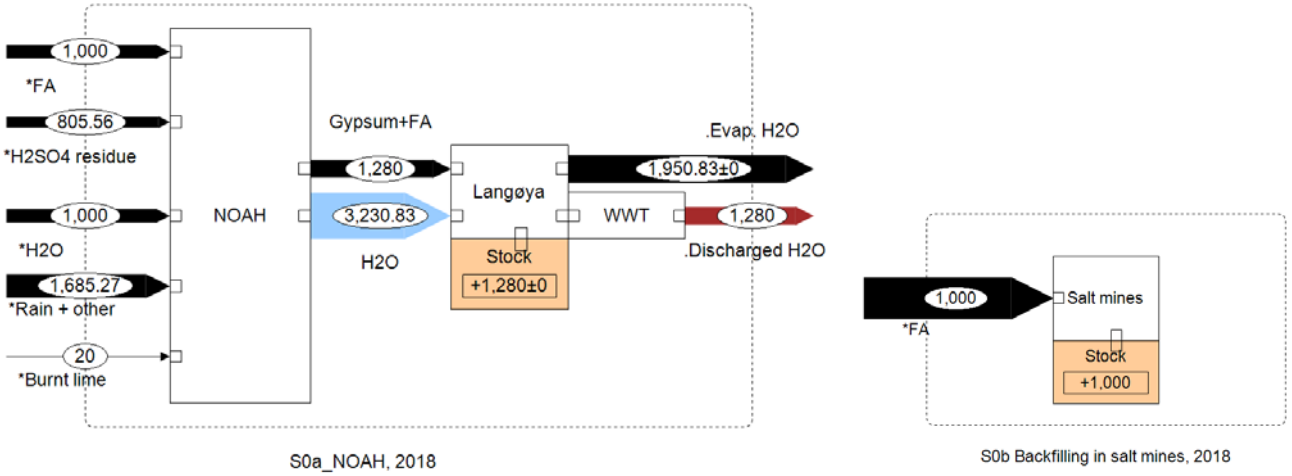


Figure A0. 100y & 500y. Scenarios S0a (NOAH process, Norway) and S0b (backfilling material in German salt mines). Scenario S0a, to the left, and Scenario S0b, to the right, are representative of both time horizon 100y and 500y.

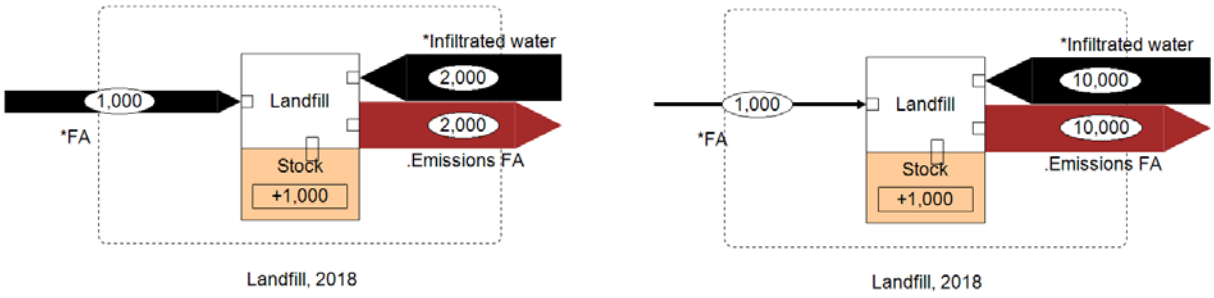


Figure A1. 100y & 500y. Scenario S1 (Landfill without pre-treatment) considering a time horizon of 100y to the left and 500y to the right.

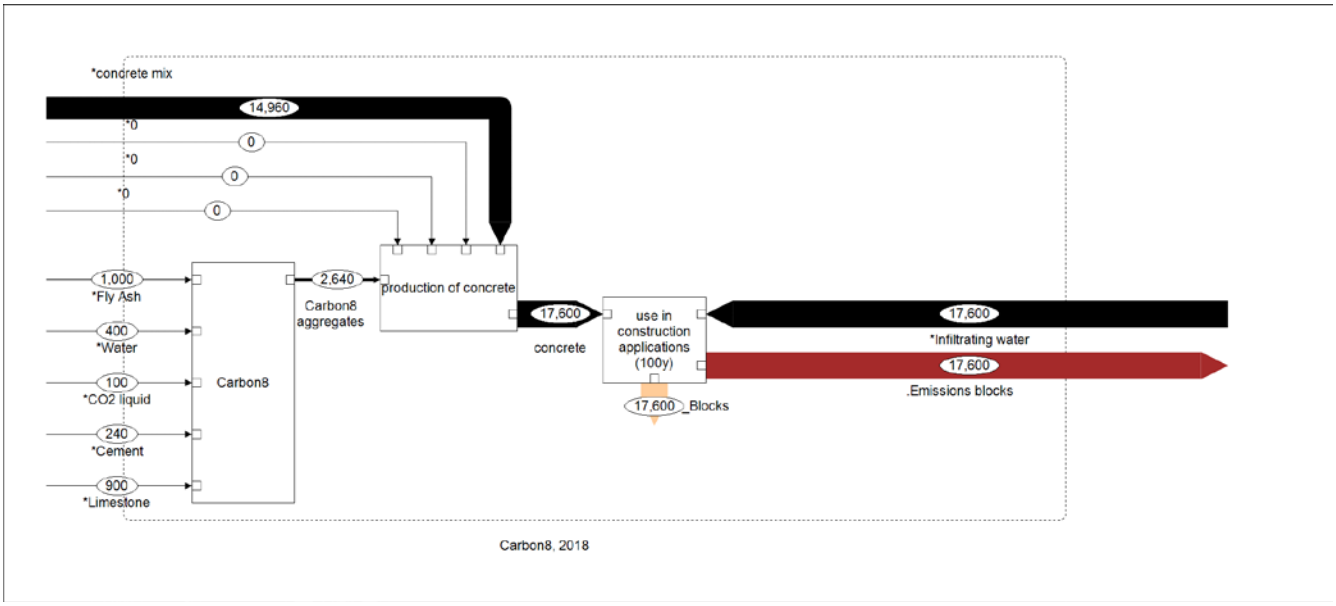


Figure A2.100y Scenario S2 (Carbon8) considering a time horizon of 100y.

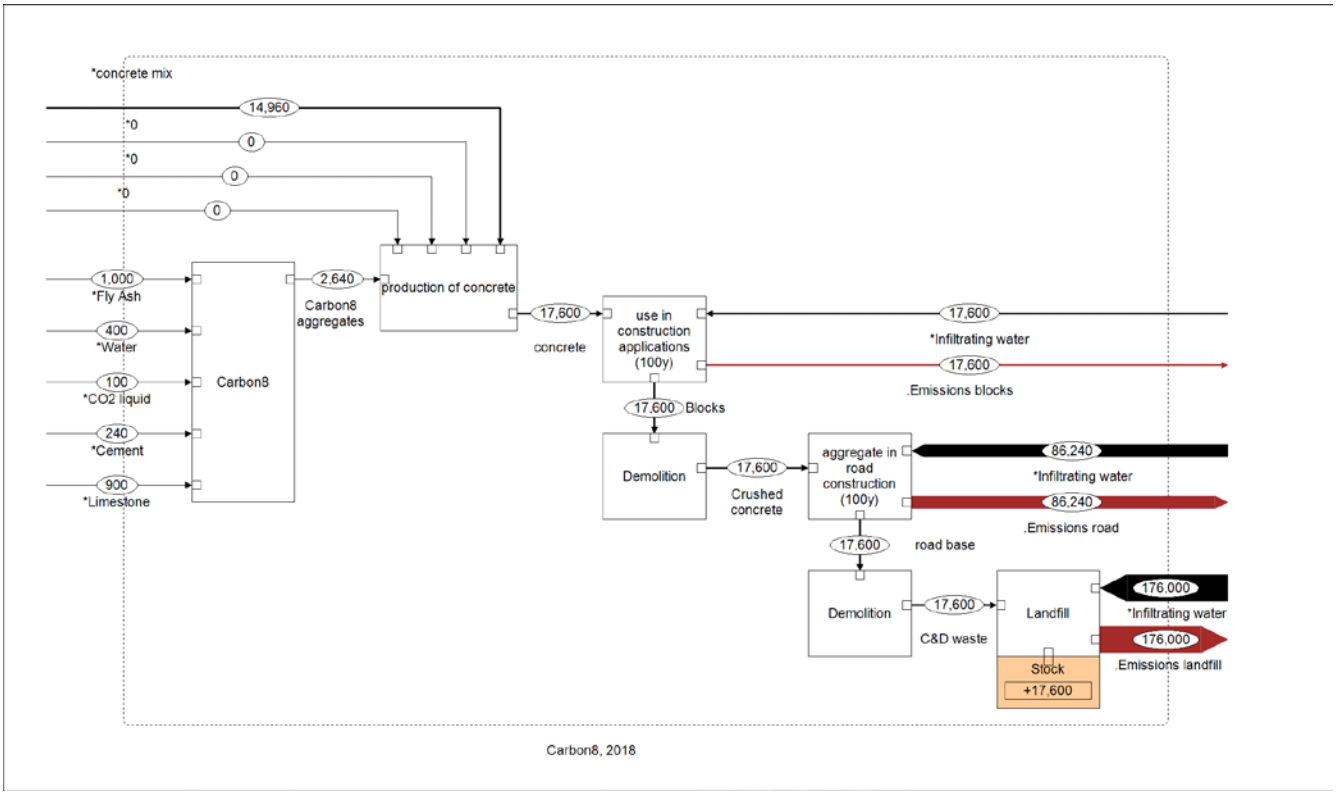


Figure A2.500y Scenario S2 (Carbon8) considering a time horizon of 500y.

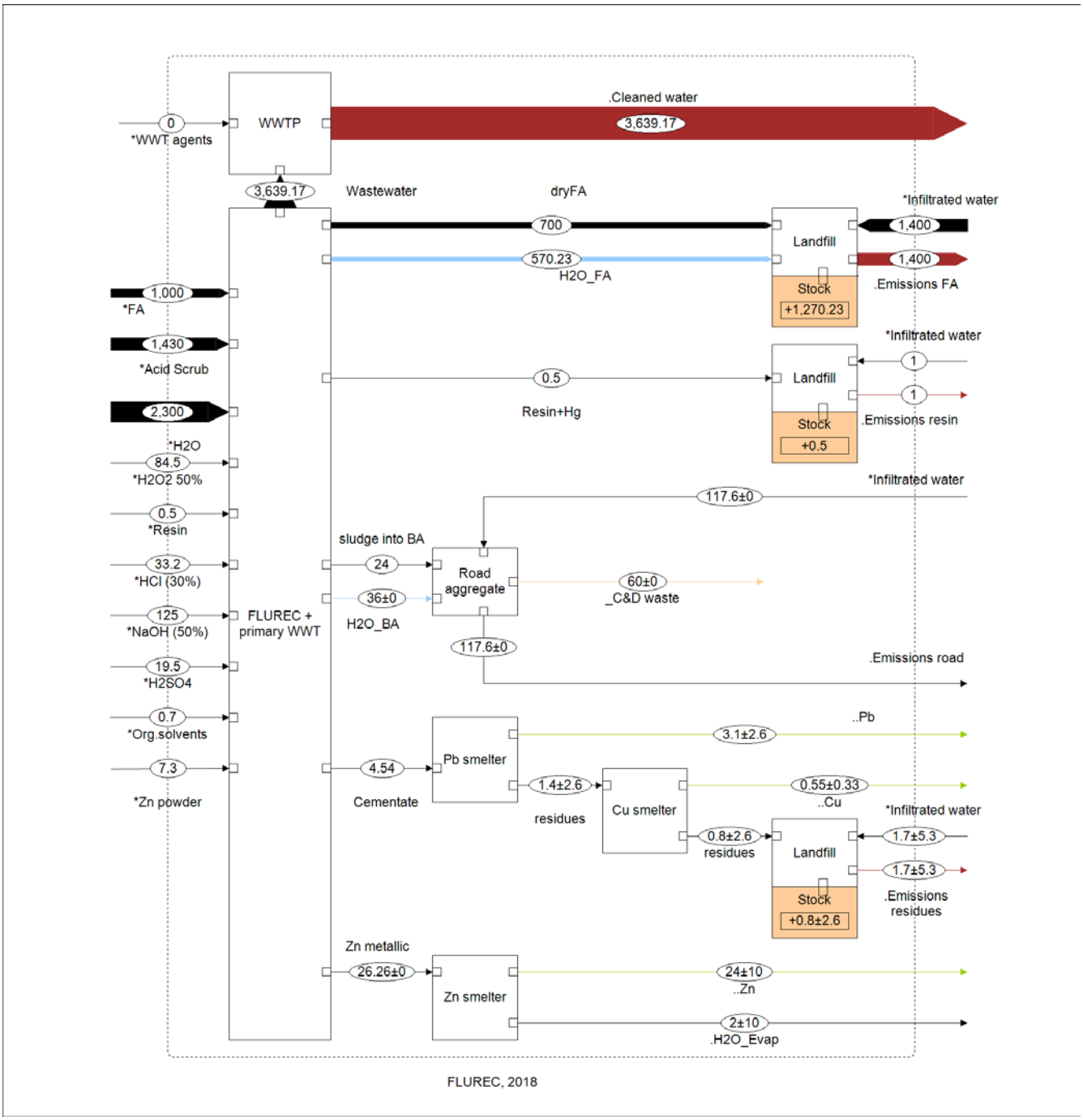


Figure A3.100y Scenario S3+Cu (Flurec) considering a time horizon of 100y.

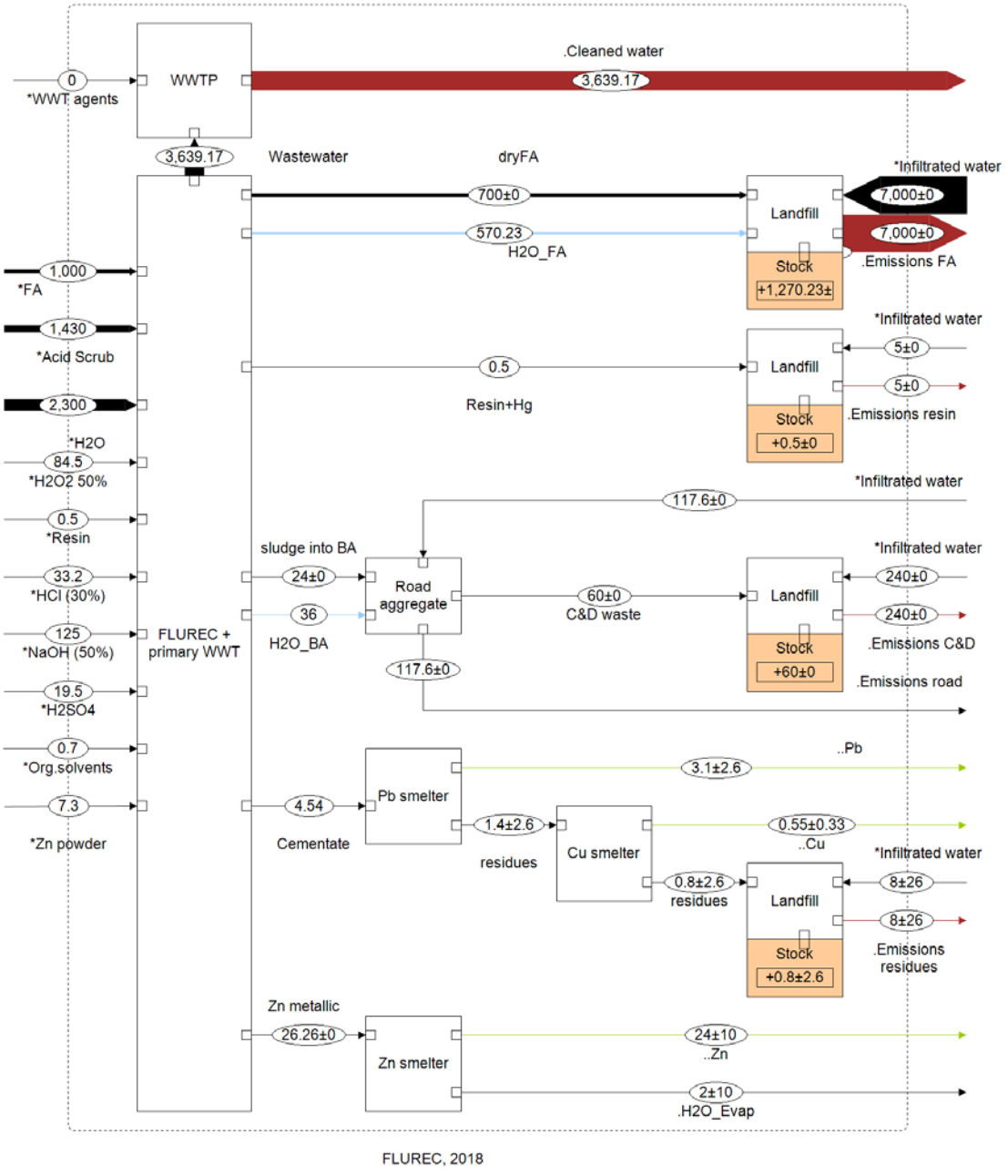


Figure A3.500y Scenario S3+Cu (Flurec) considering a time horizon of 500y.

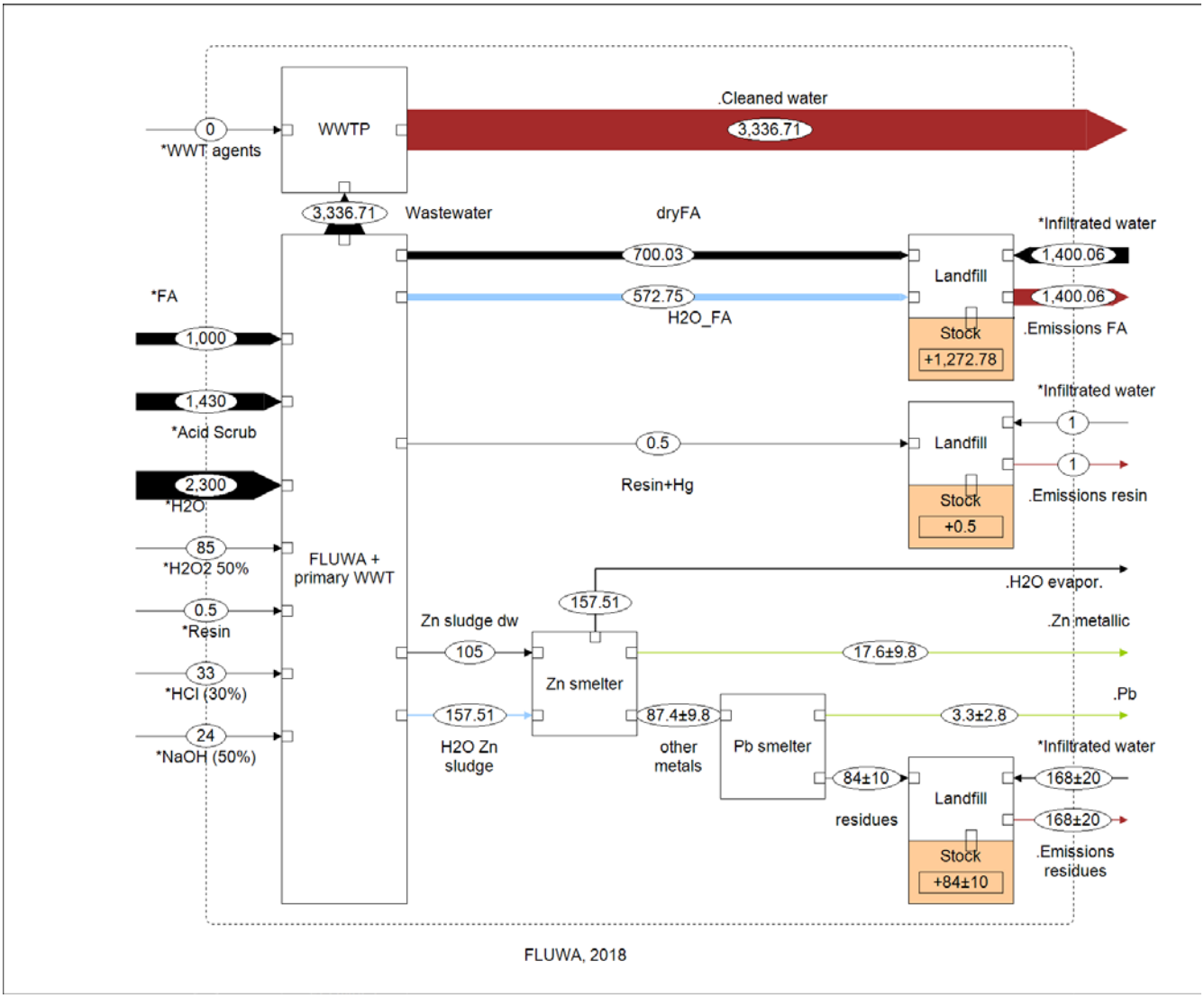


Figure A4.100y Scenario S4 (Fluwa) considering a time horizon of 100y.

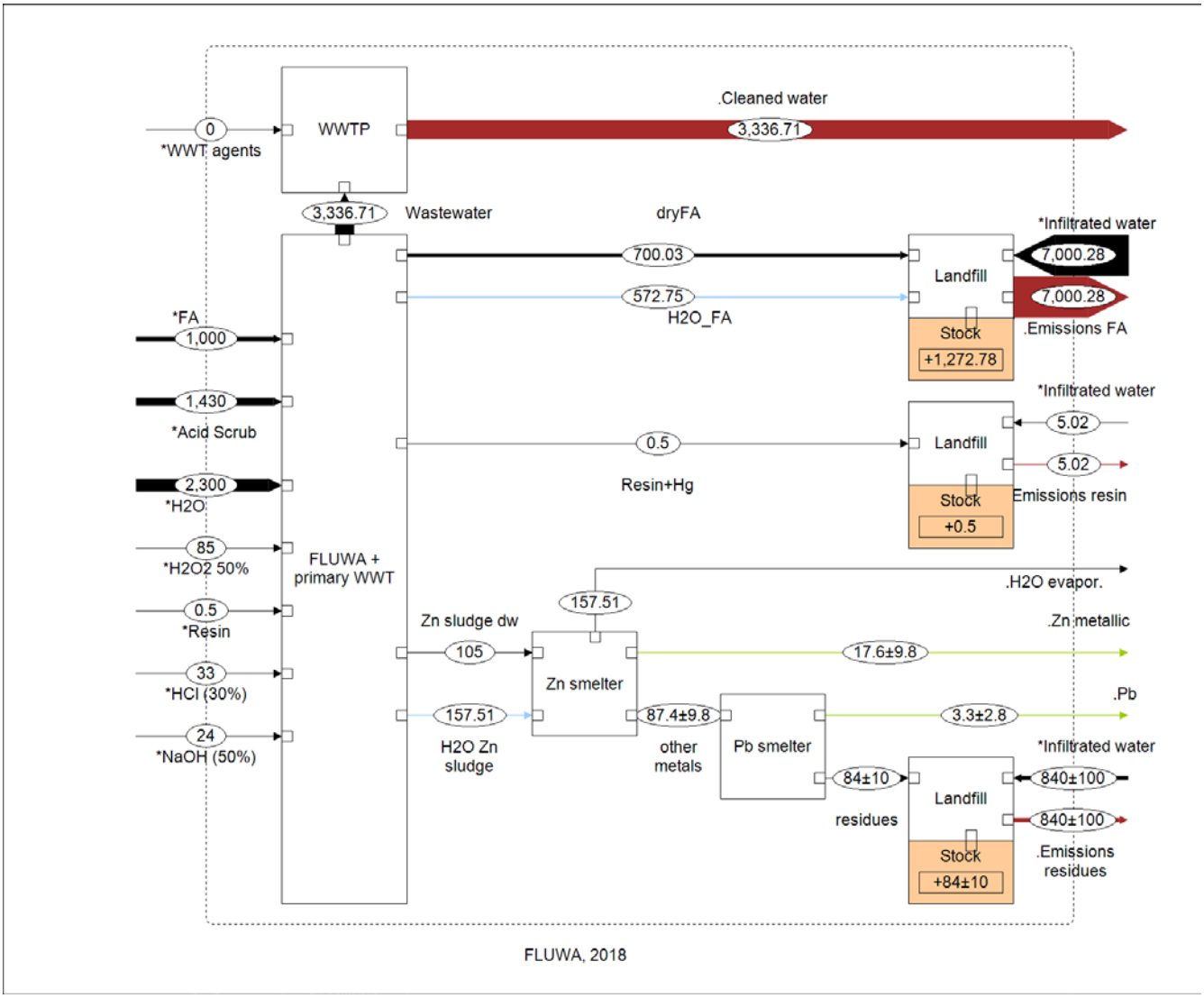


Figure A4.500y Scenario S4 (Fluwa) considering a time horizon of 500y.

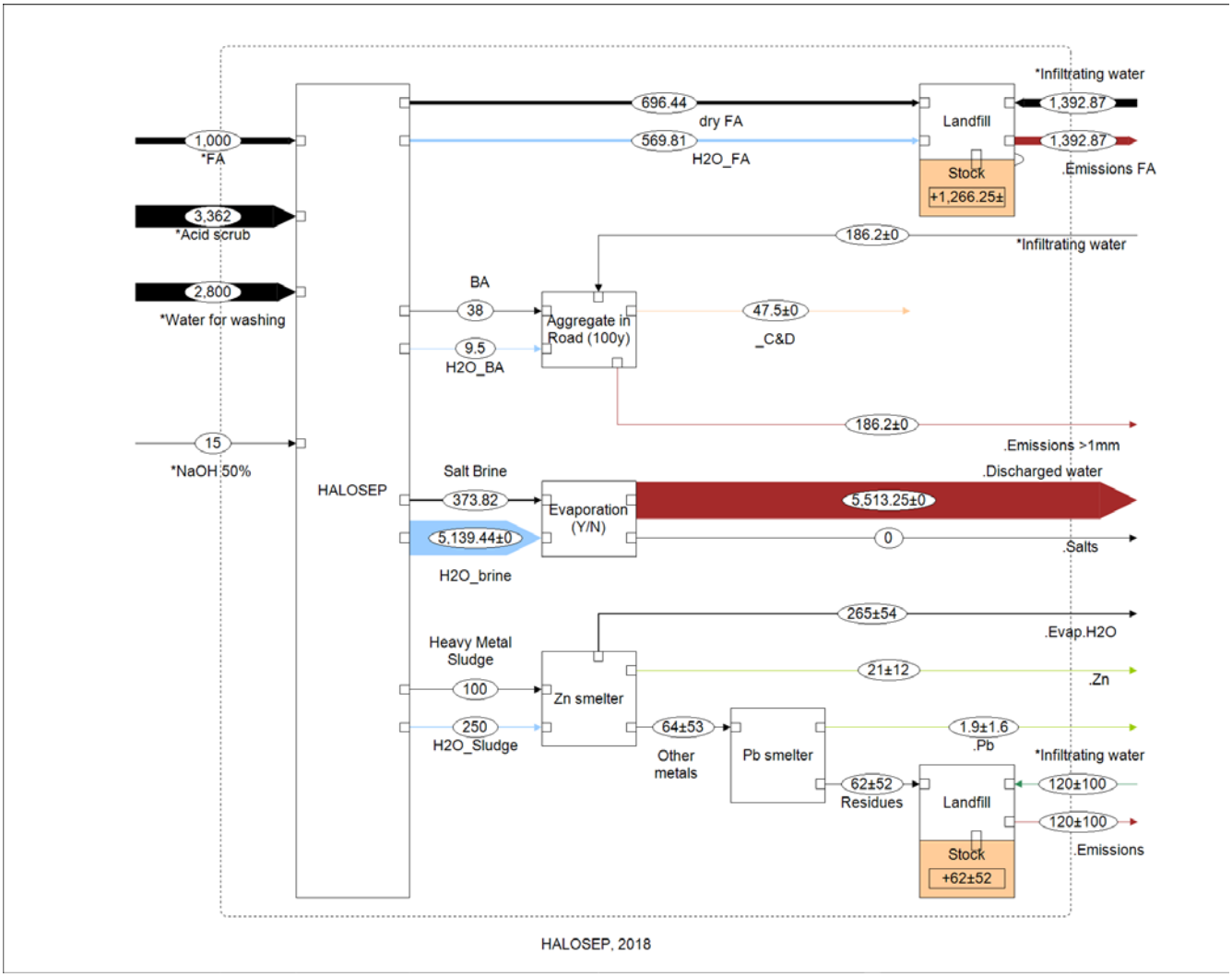


Figure A5.100y Scenario S5 (Halosep) considering a time horizon of 100y.

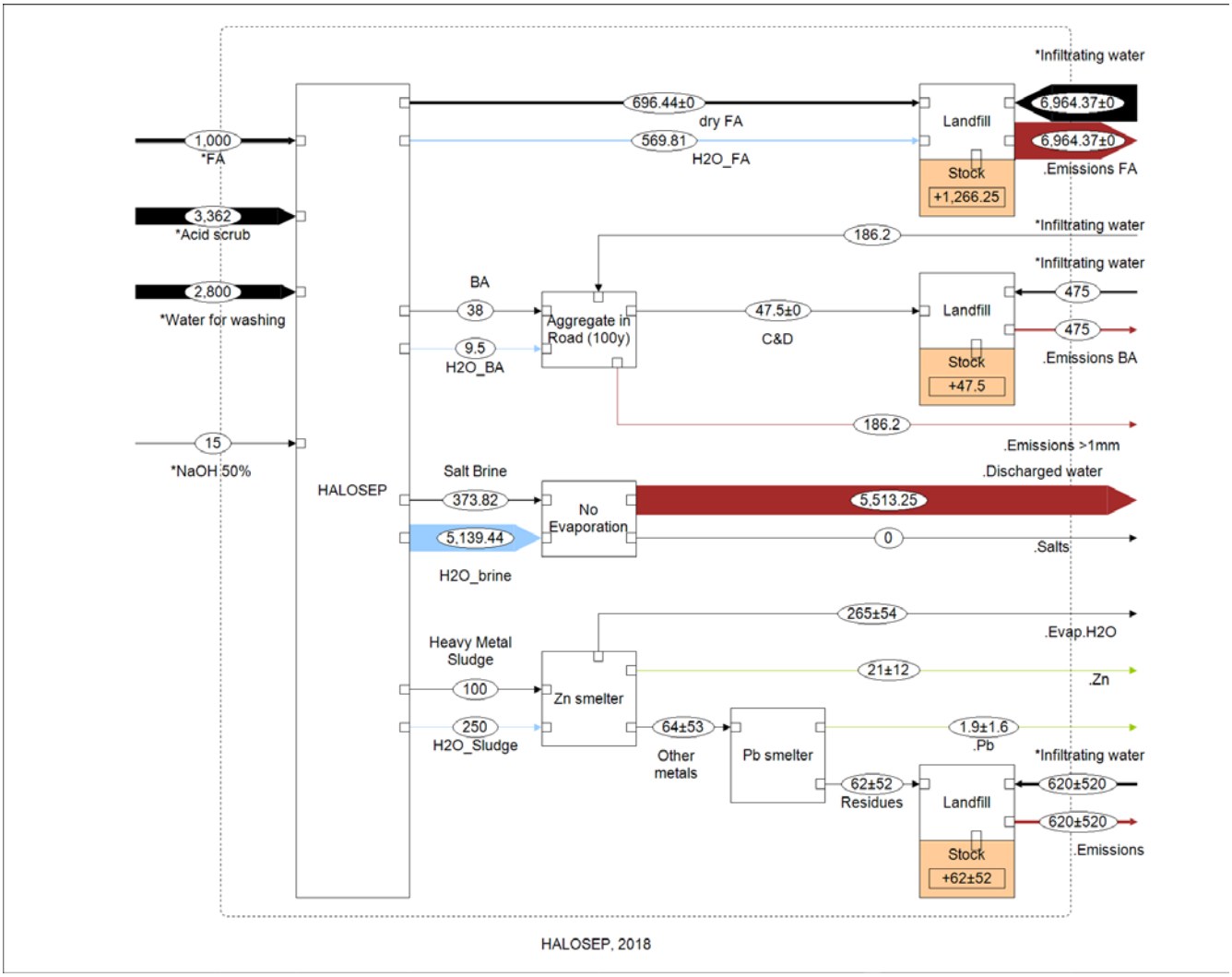


Figure A5.500y Scenario S5 (Halosep) considering a time horizon of 500y.

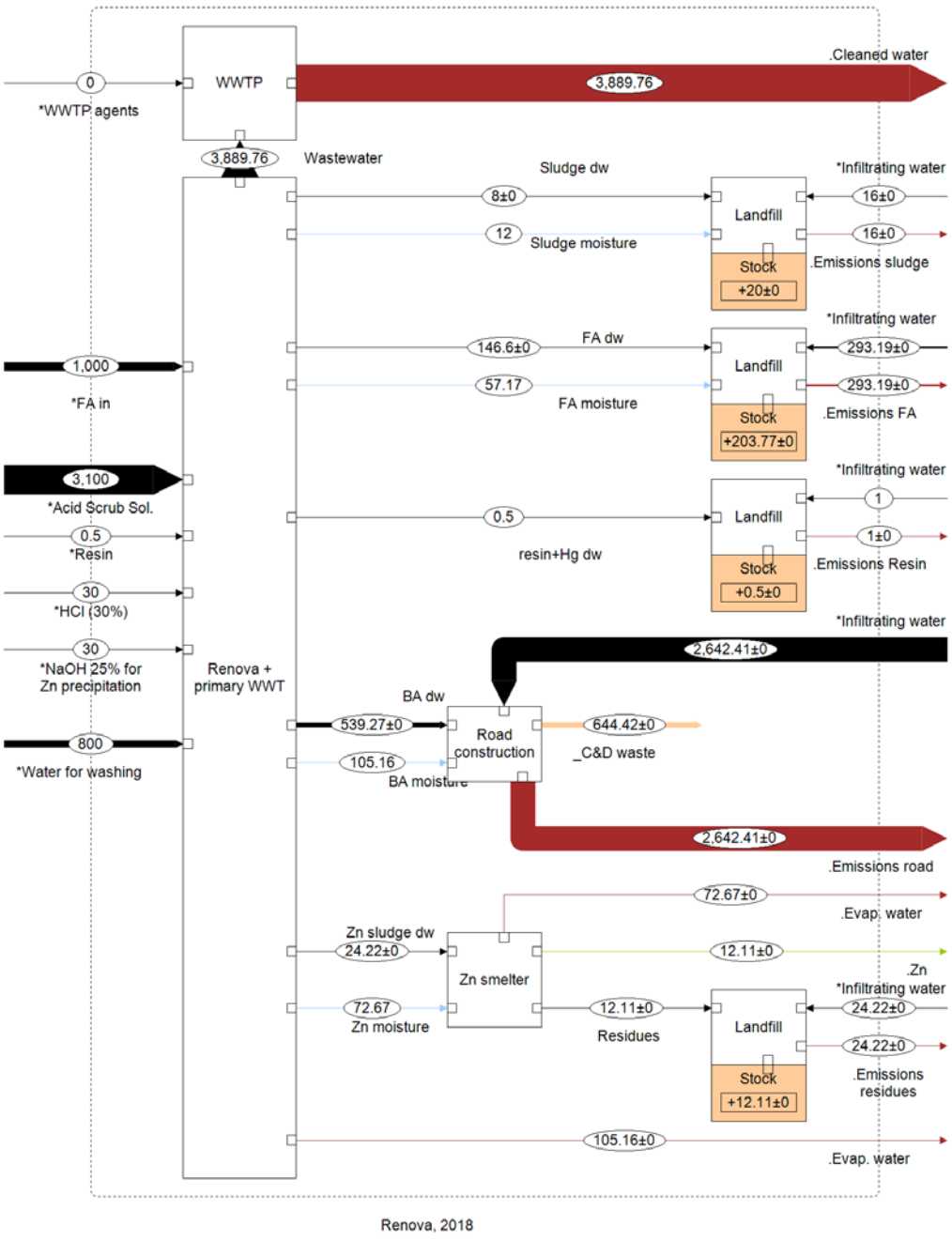


Figure A6.100y Scenario S6 (Renova) considering a time horizon of 100y.

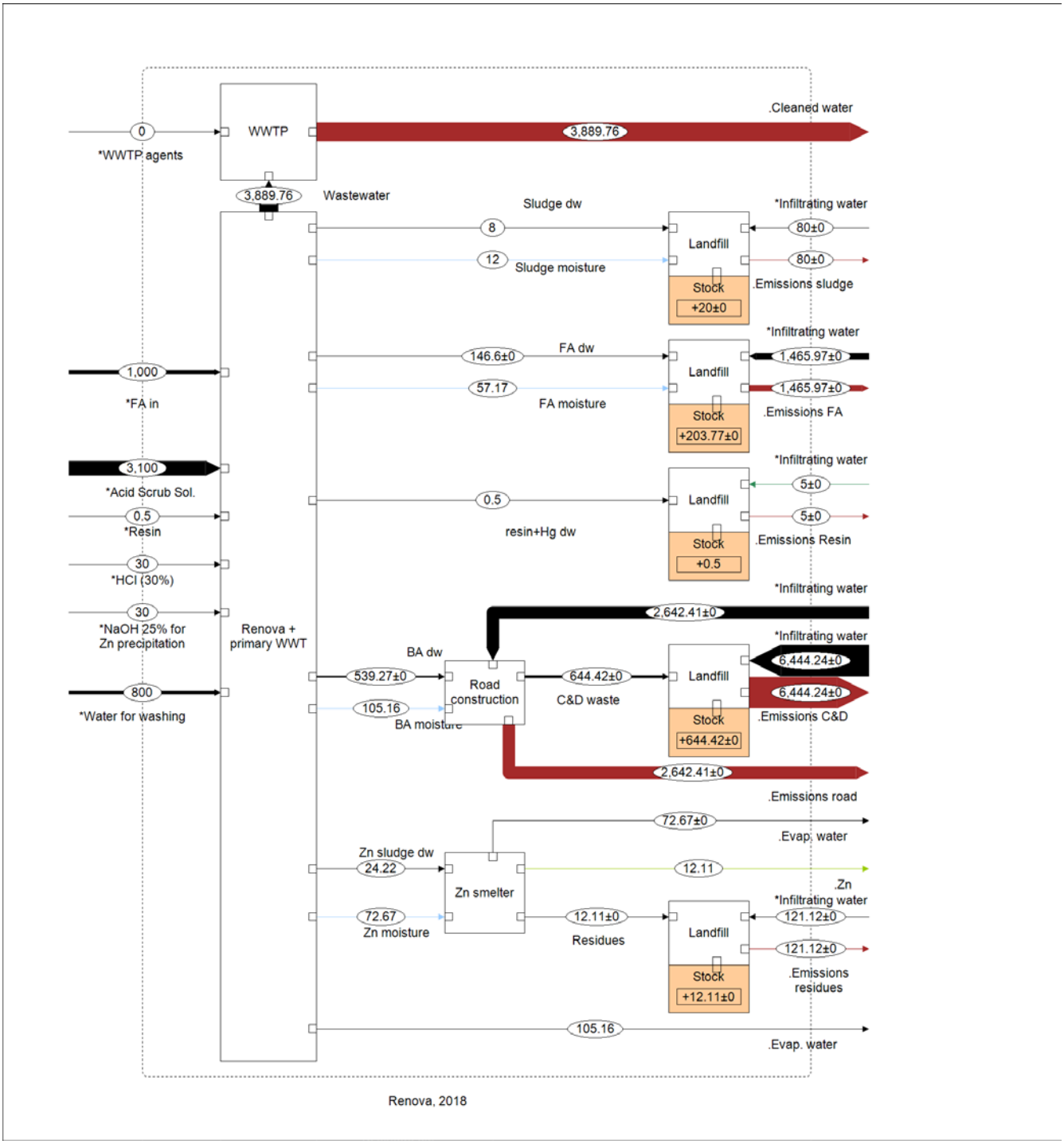


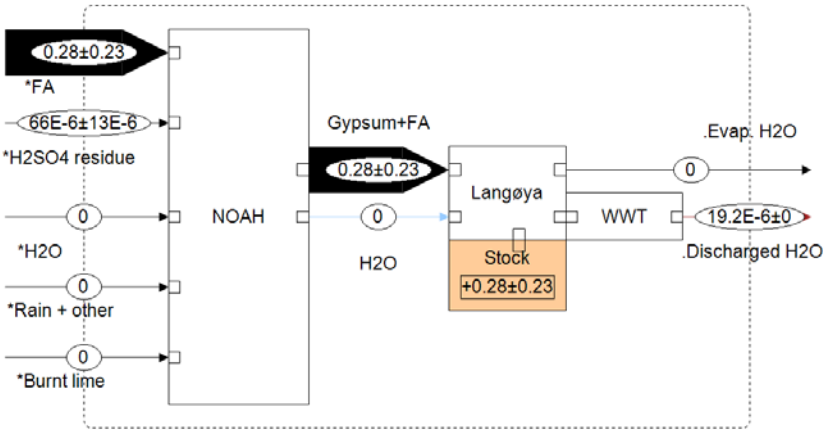
Figure A6.500y Scenario S6 (Renova) considering a time horizon of 500y.

APPENDIX B. Substance Flow Analyses of the individual scenarios – 500y

NOTE: Scenario S0b (backfilling in German salt mines) is not reported in the Appendix B figures because it is assumed that everything remains stored in the salt mines – see Figure S0b in Appendix A.

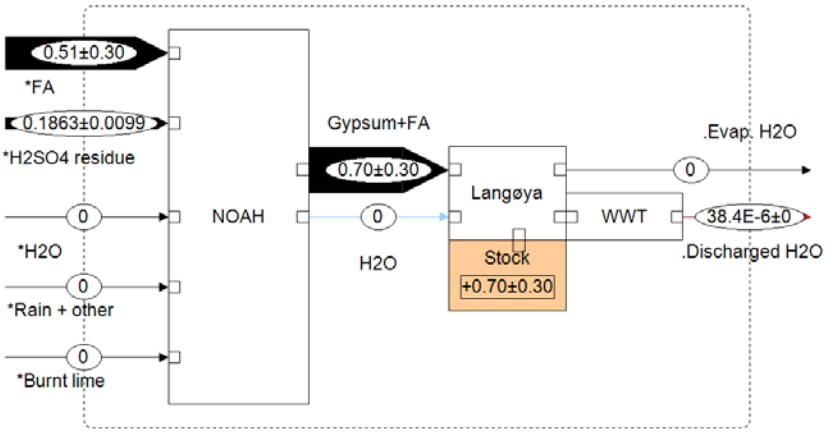
Scenario S0a (NOAH process), 500y

- **As (figure below)**



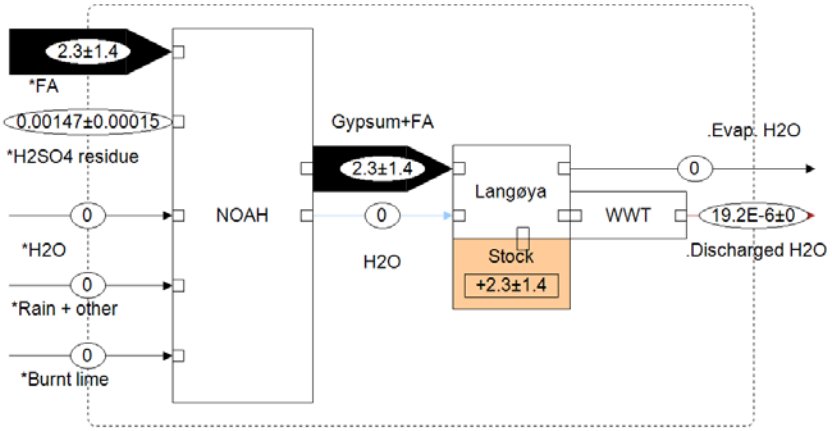
S0a_NOAH, 2018

- **Cr (figure below)**



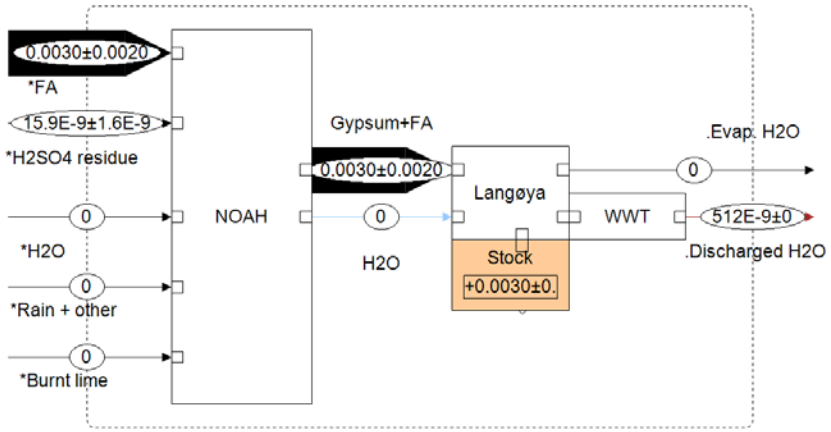
S0a_NOAH, 2018

- **Cu (figure below)**



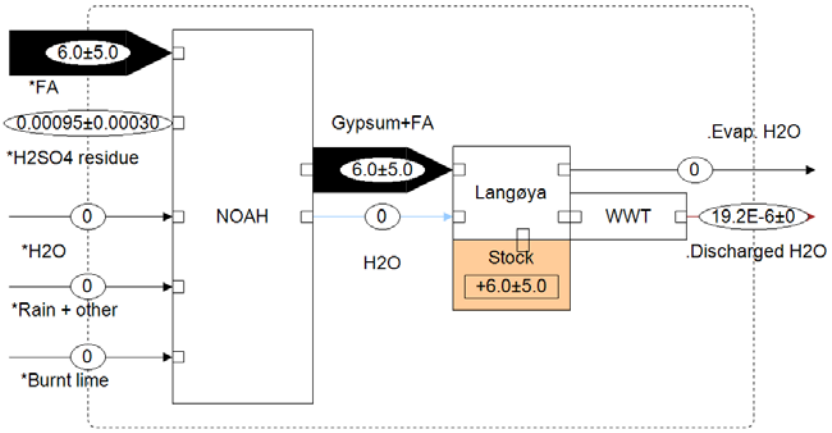
S0a_NOAH, 2018

- **Hg (figure below)**



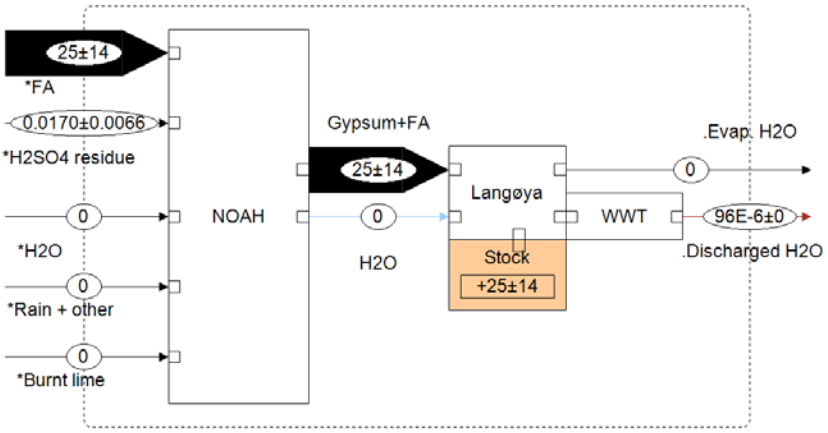
S0a_NOAH, 2018

- **Pb (figure below)**



S0a_NOAH, 2018

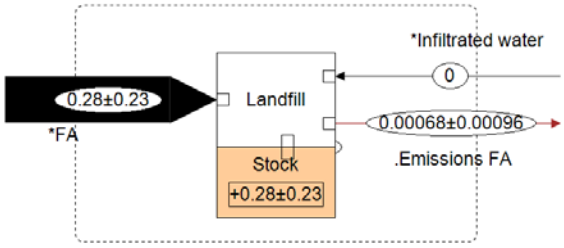
- **Zn (figure below)**



S0a_NOAH, 2018

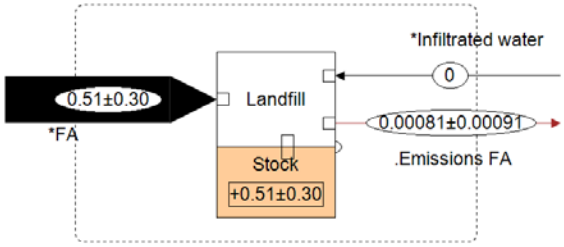
Scenario S1 (Landfill without pre-treatments), 500y

- **As (figure below)**



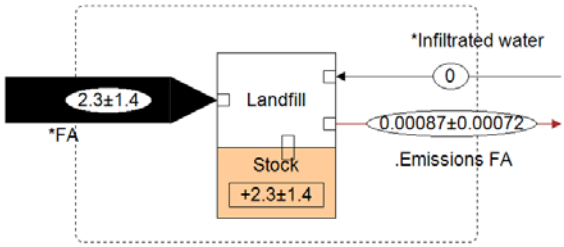
Landfill, 2018

- **Cr (figure below)**



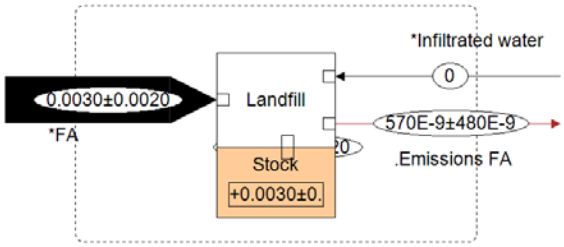
Landfill, 2018

- **Cu (figure below)**



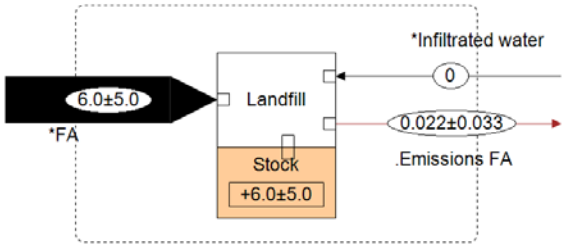
Landfill, 2018

- **Hg (figure below)**



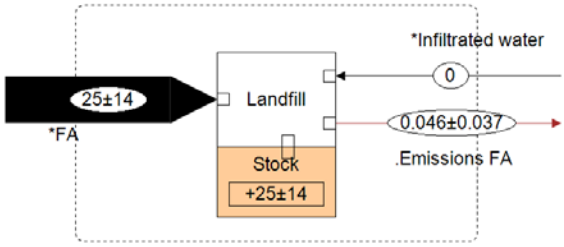
Landfill, 2018

- **Pb (figure below)**



Landfill, 2018

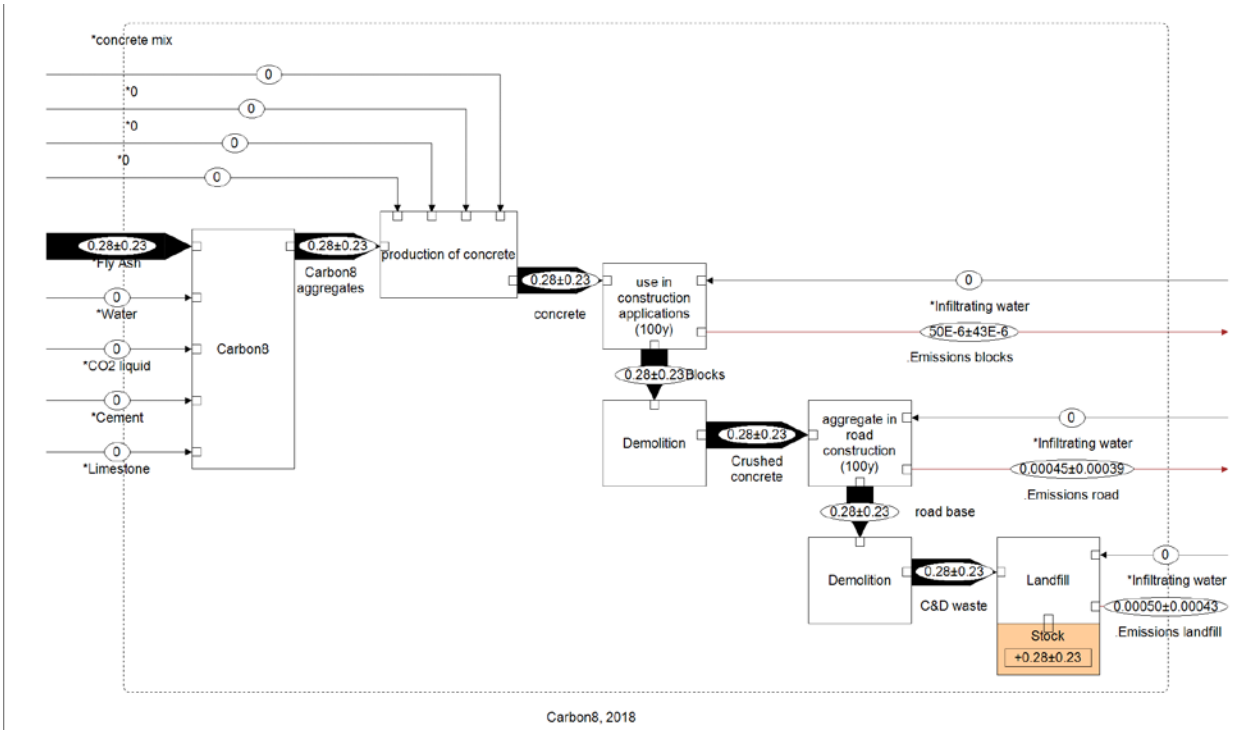
- **Zn (figure below)**



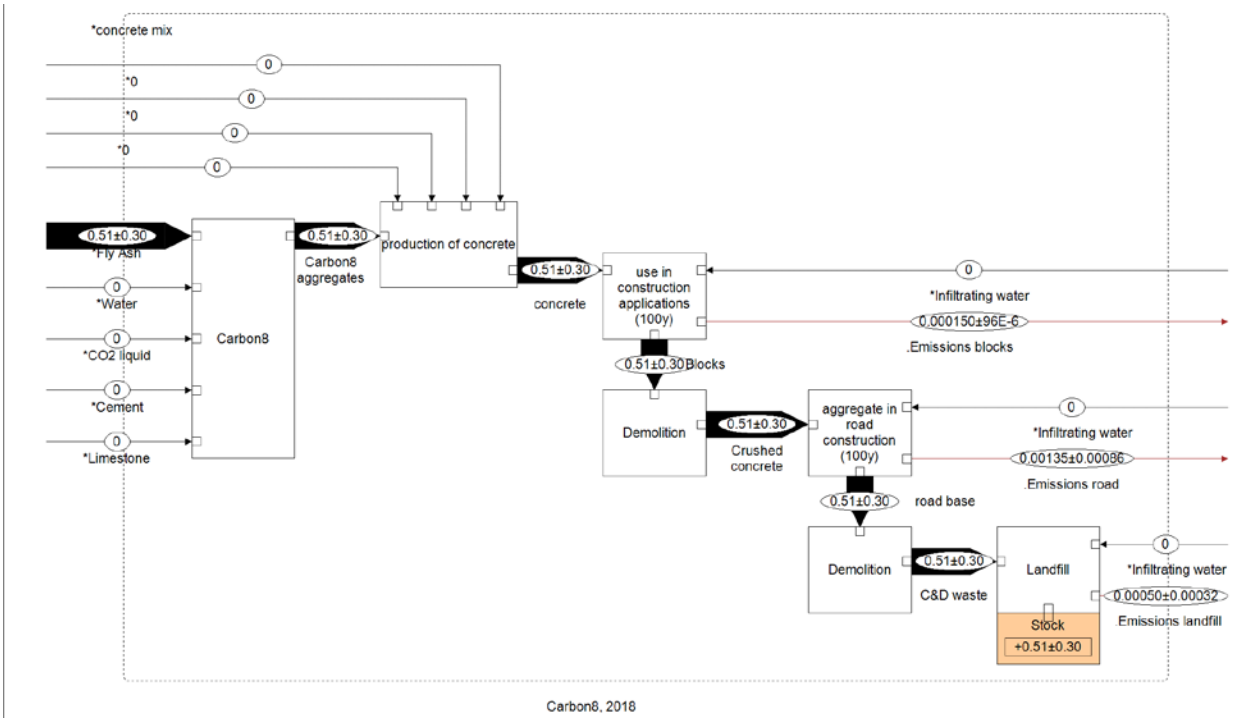
Landfill, 2018

Scenario S2 (Carbon8), 500y

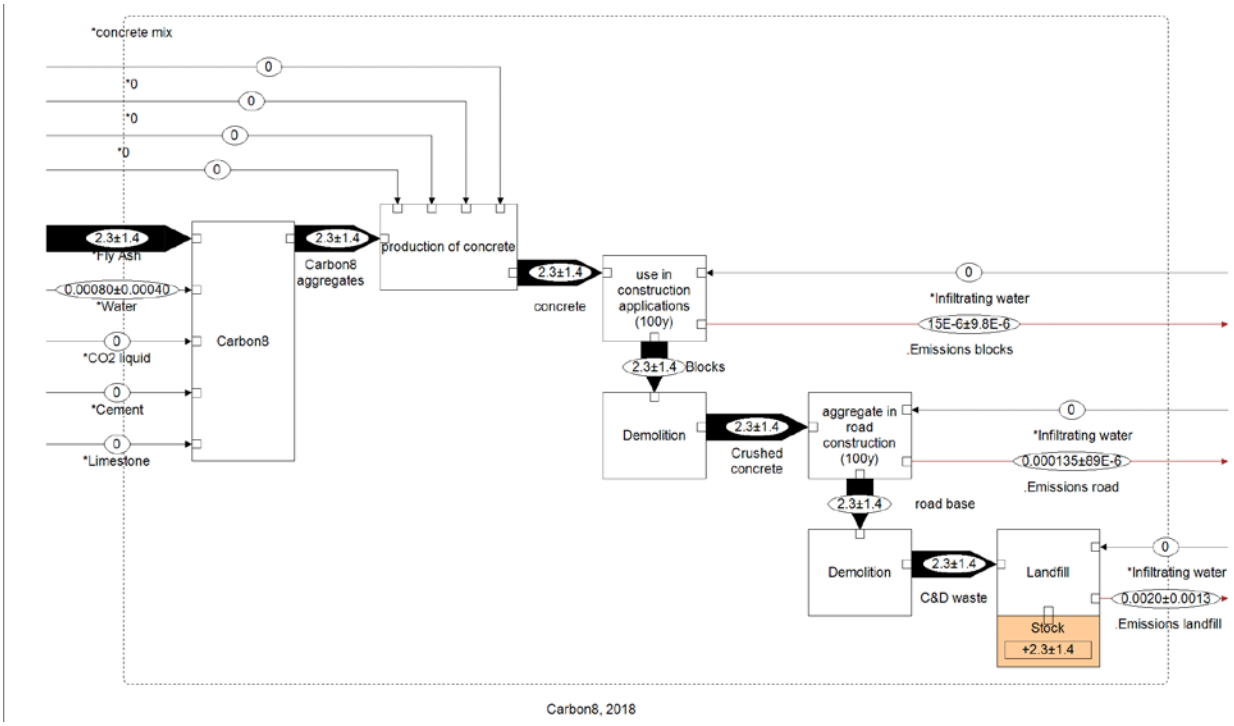
- **As (figure below)**



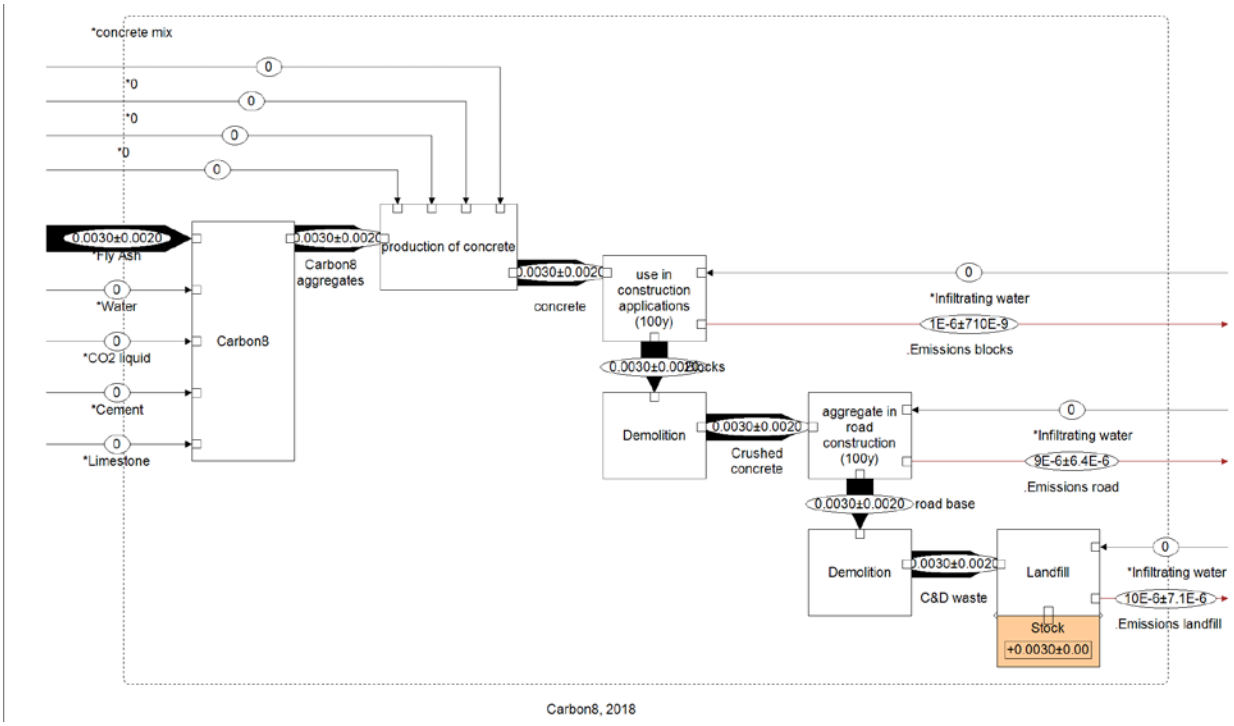
- **Cr (figure below)**



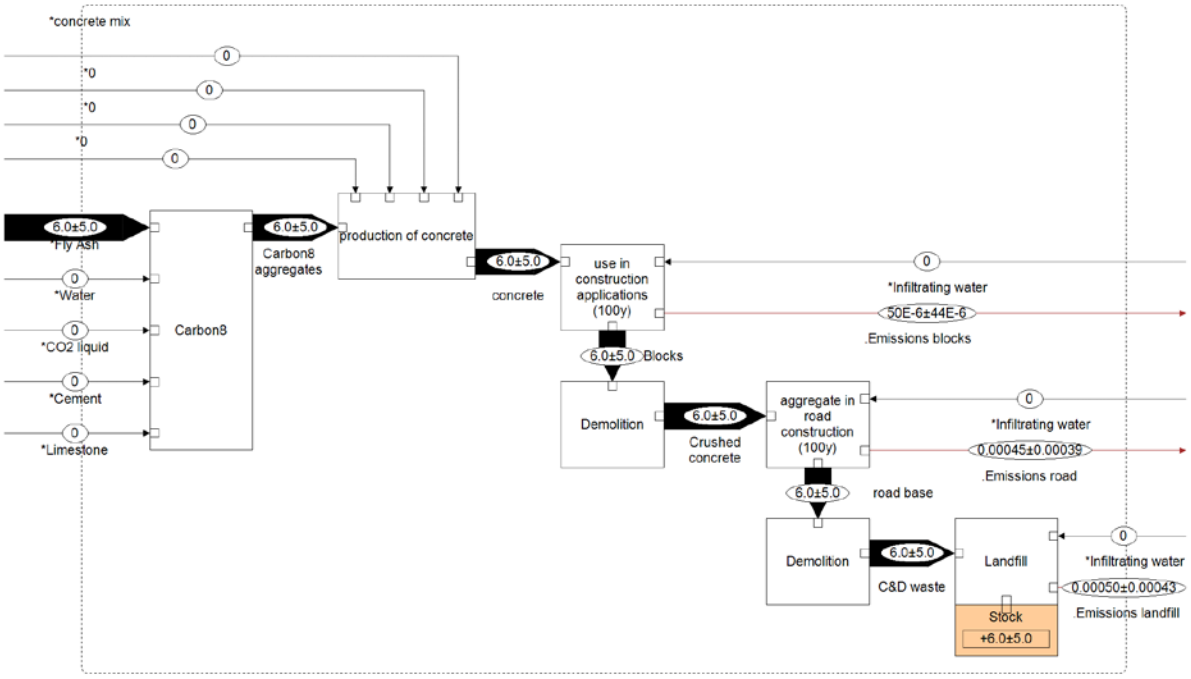
- **Cu (figure below)**



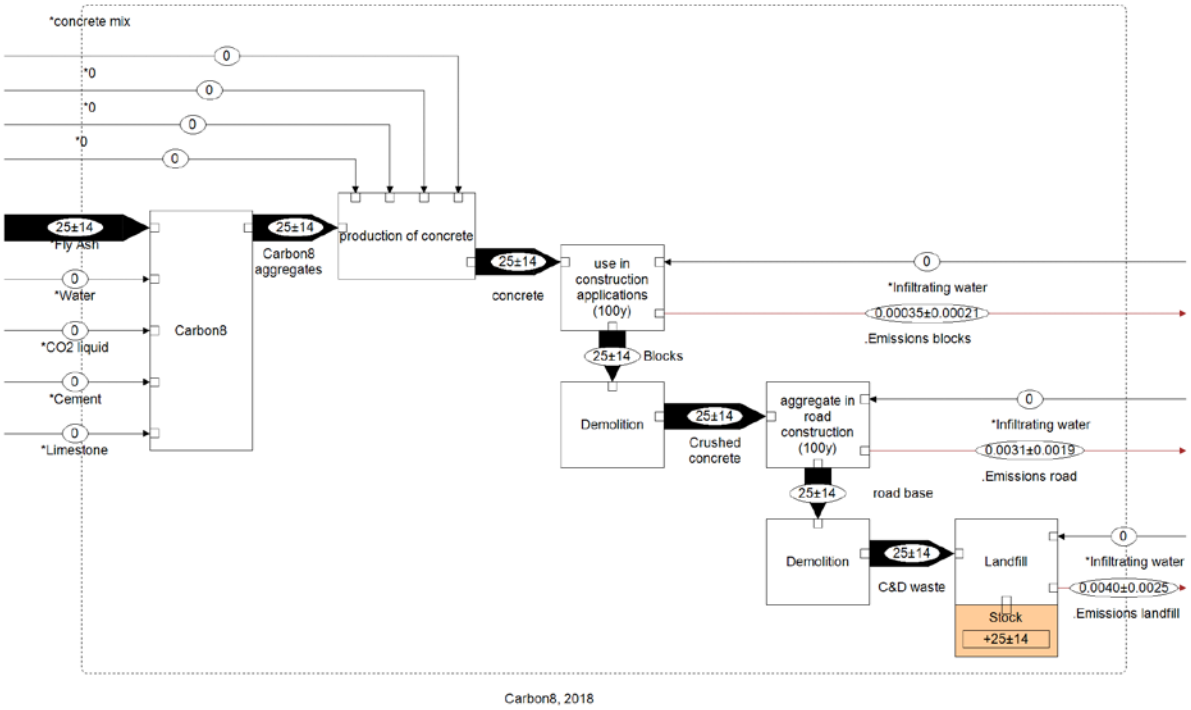
- **Hg (figure below)**



- **Pb (figure below)**

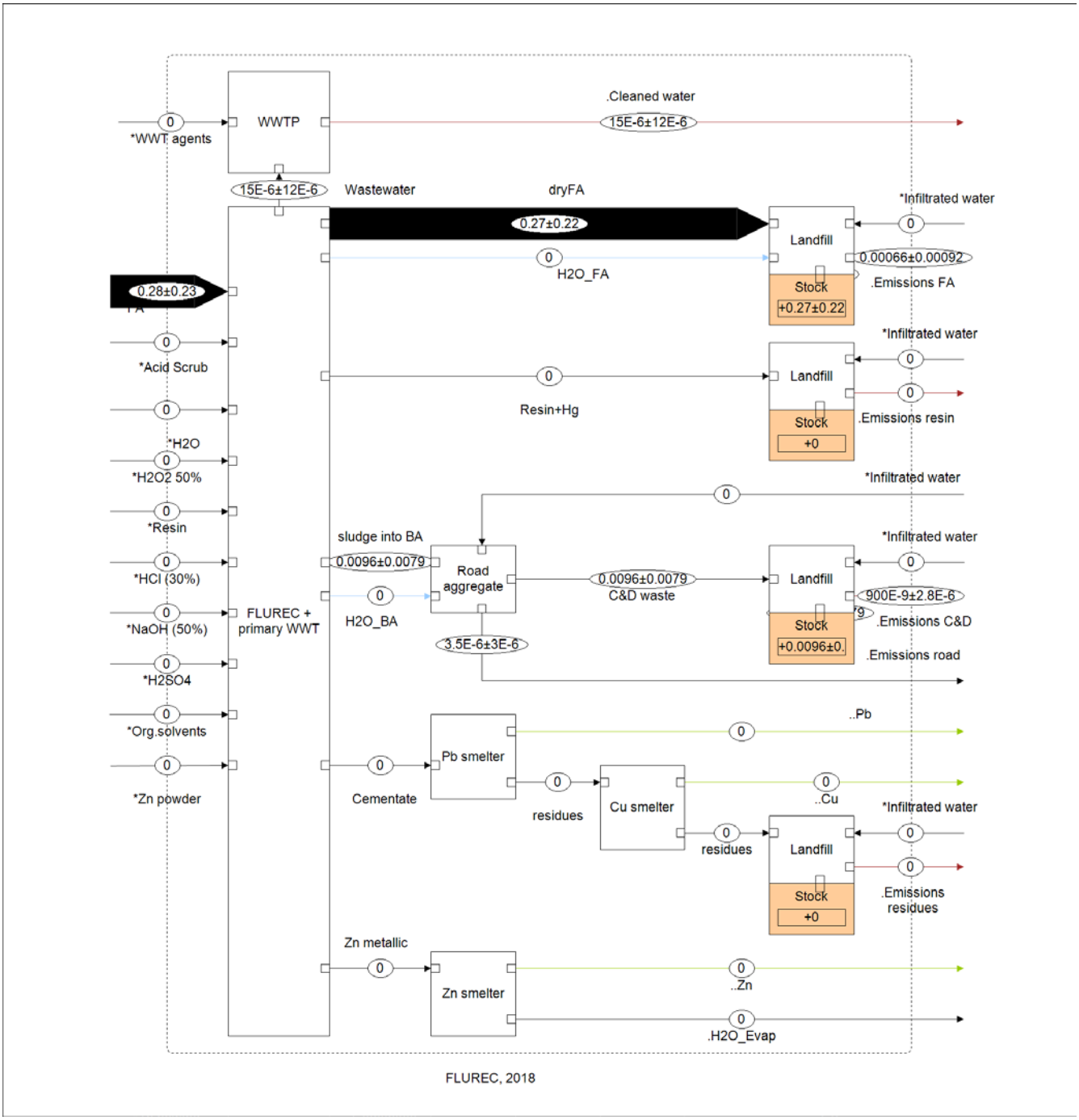


- **Zn (figure below)**

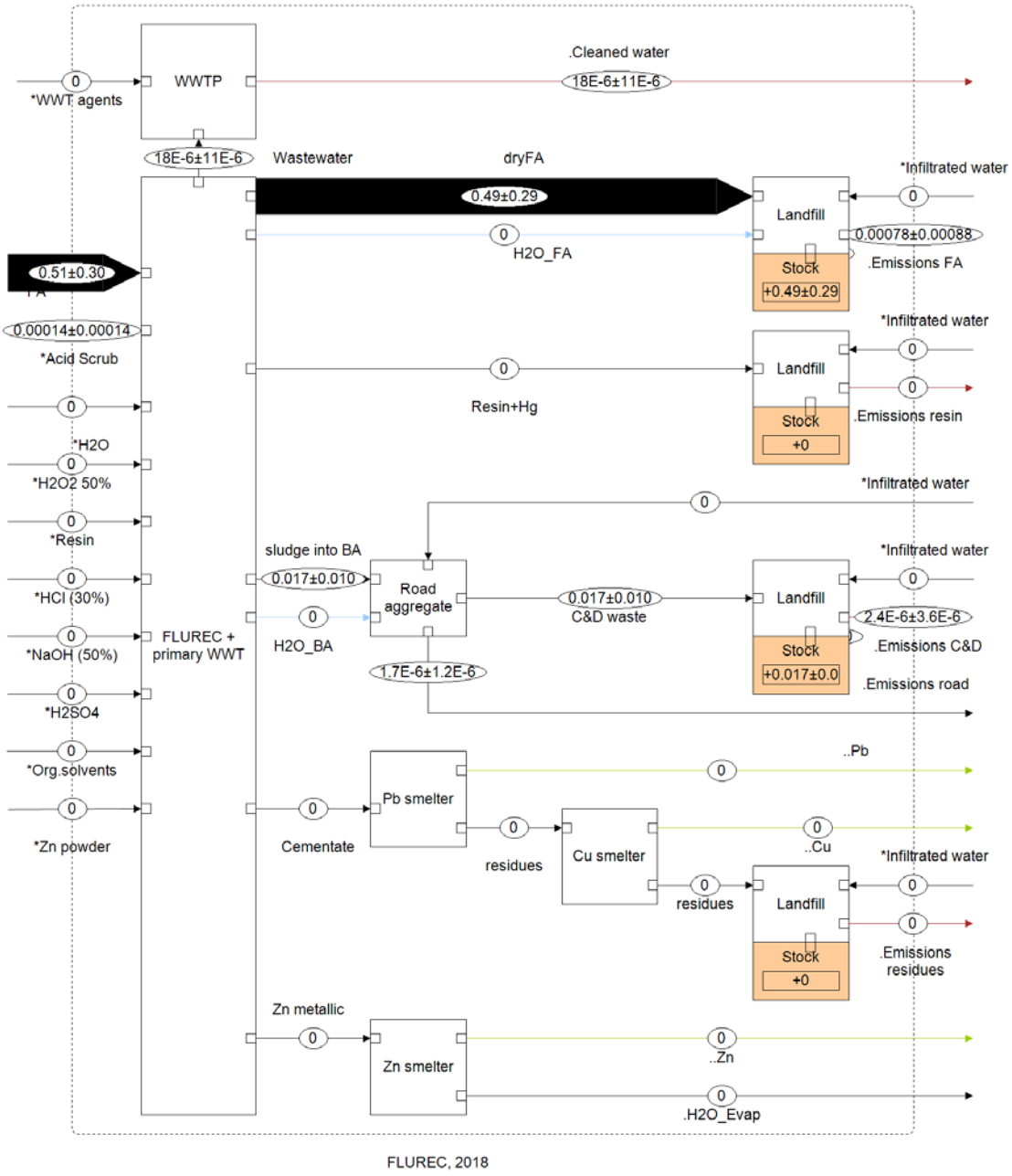


Scenario S3+Cu (Flurec), 500y

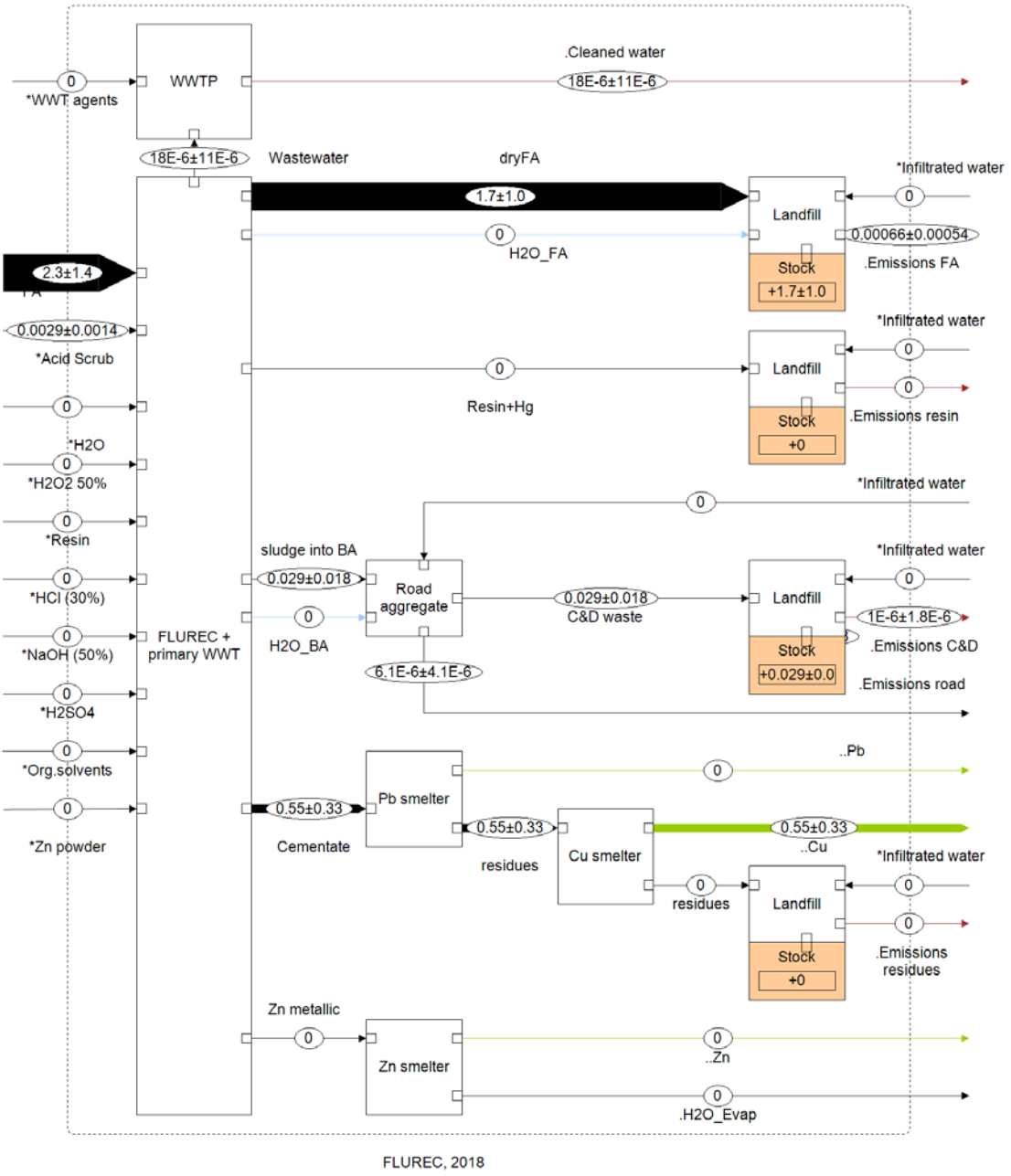
- **As (figure below)**



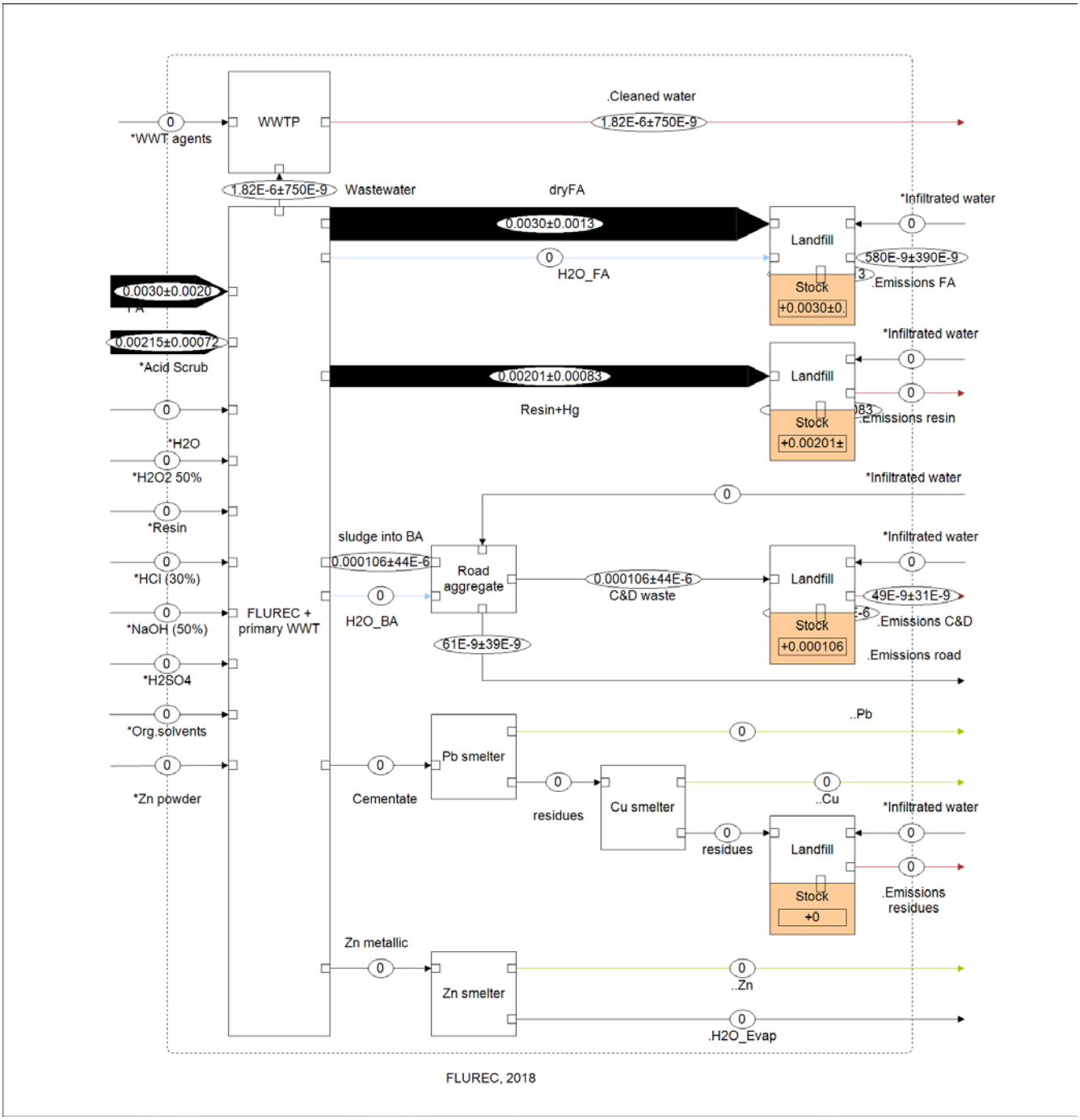
- **Cr (figure below)**



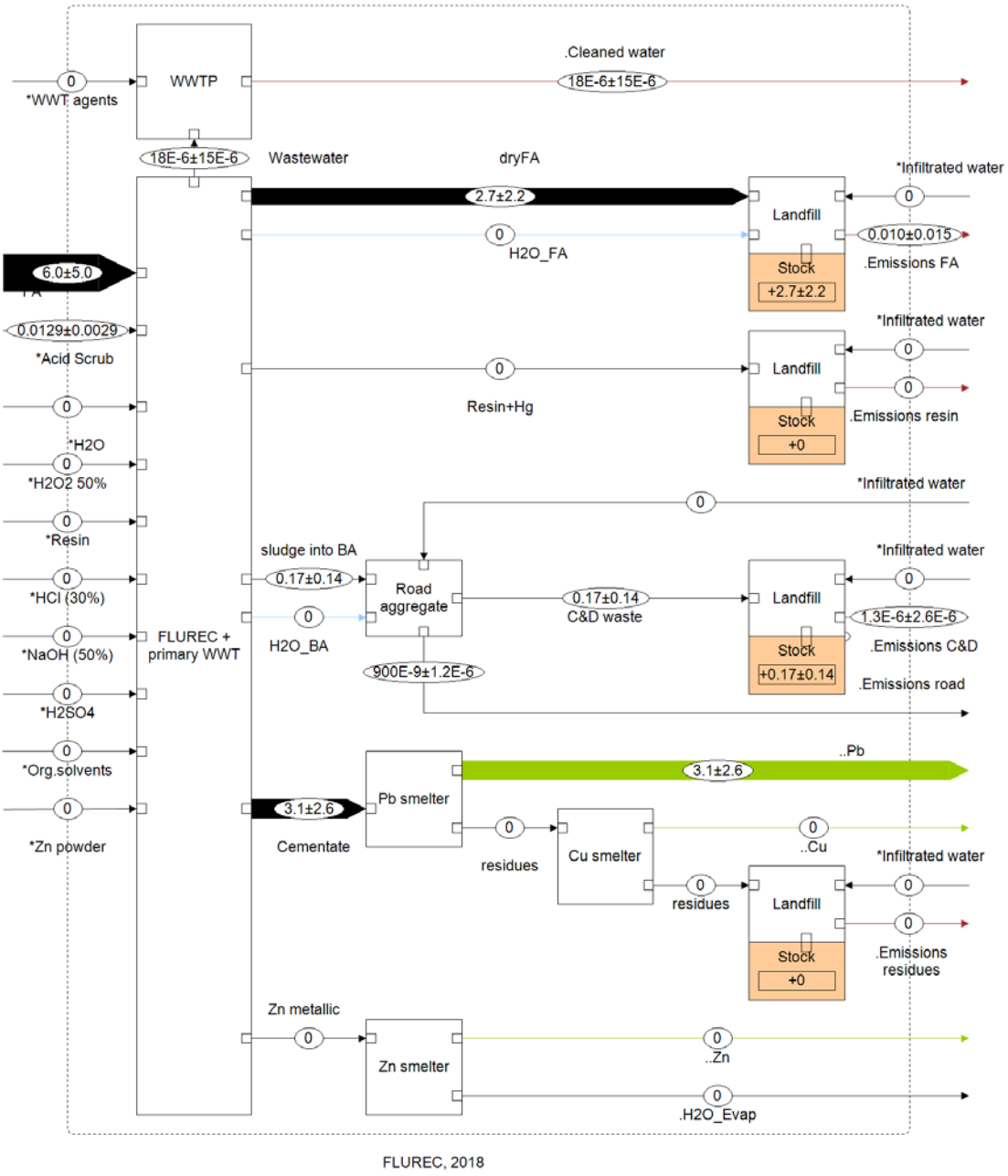
- **Cu (figure below)**



- **Hg (figure below)**

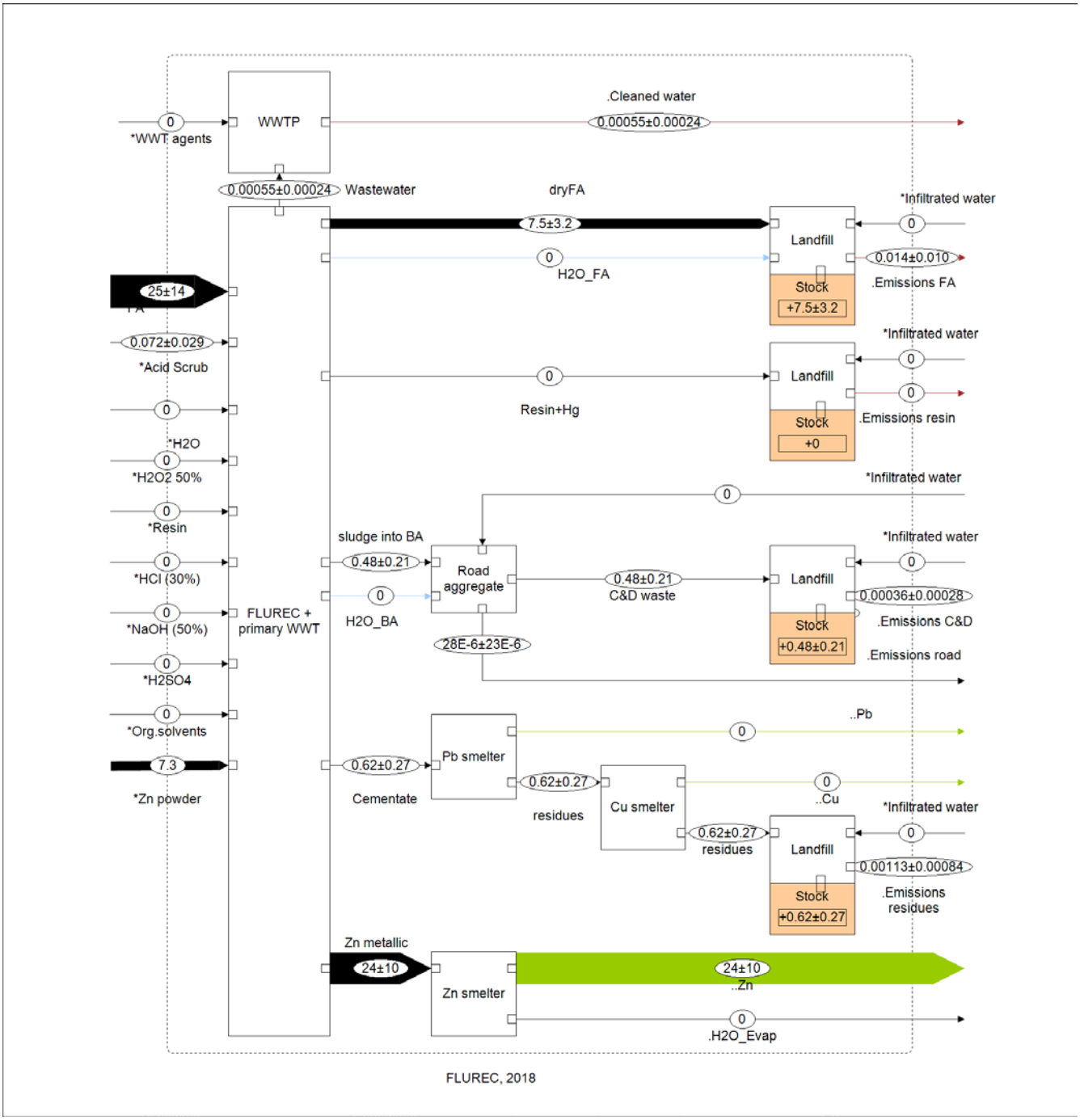


- **Pb (figure below)**



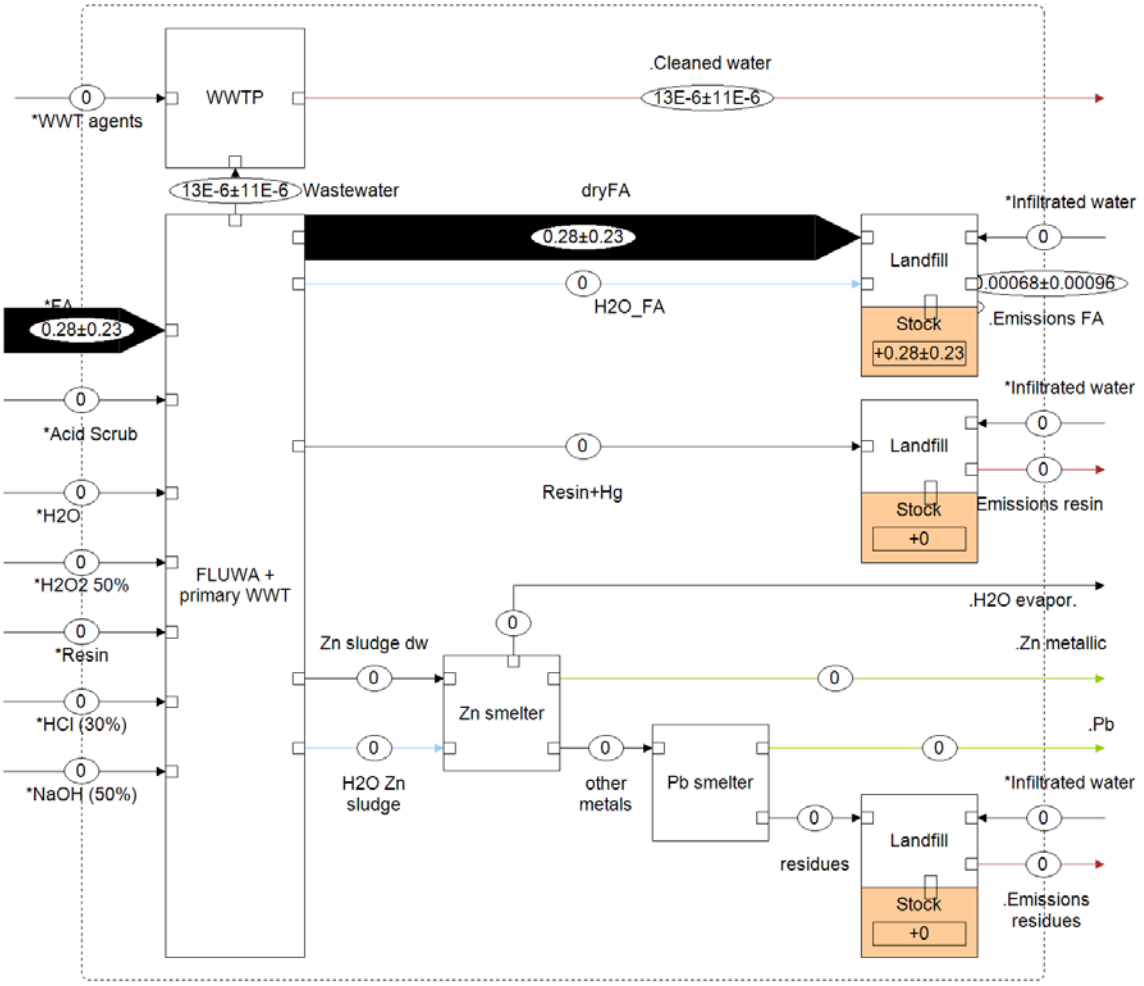
FLUREC, 2018

- **Zn (figure below)**

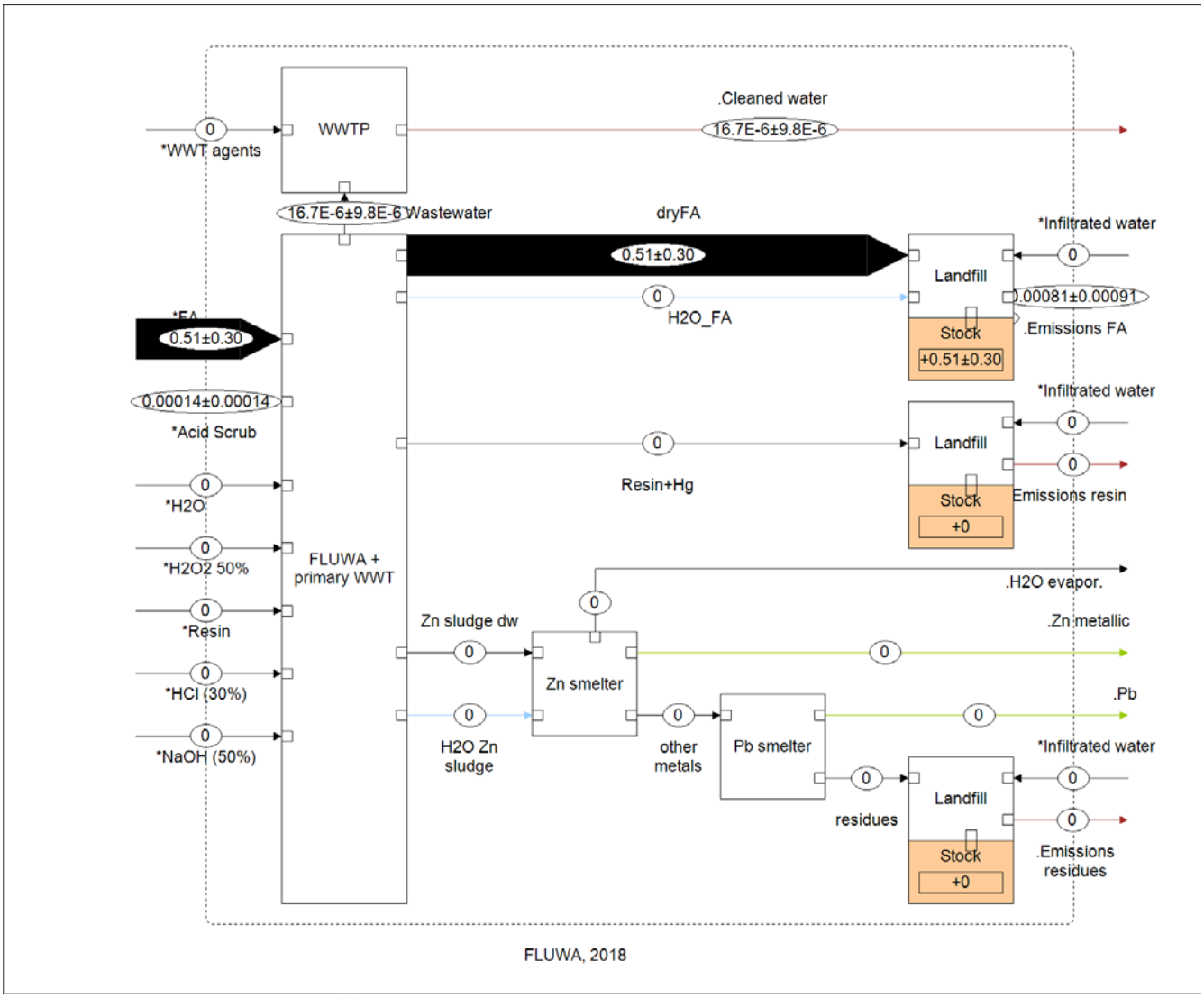


Scenario S4 (Fluwa), 500y

- **As (figure below)**

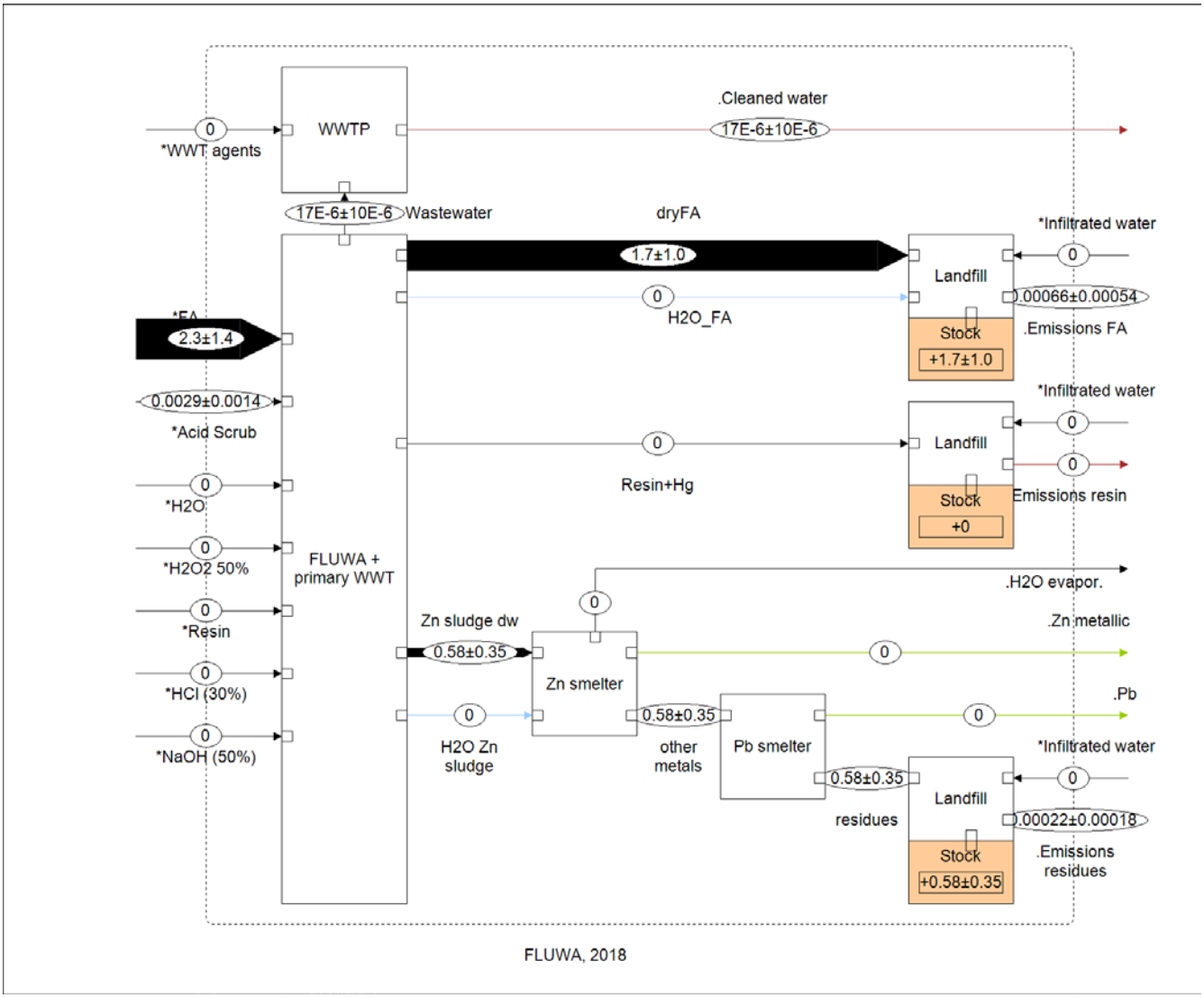


- **Cr (figure below)**

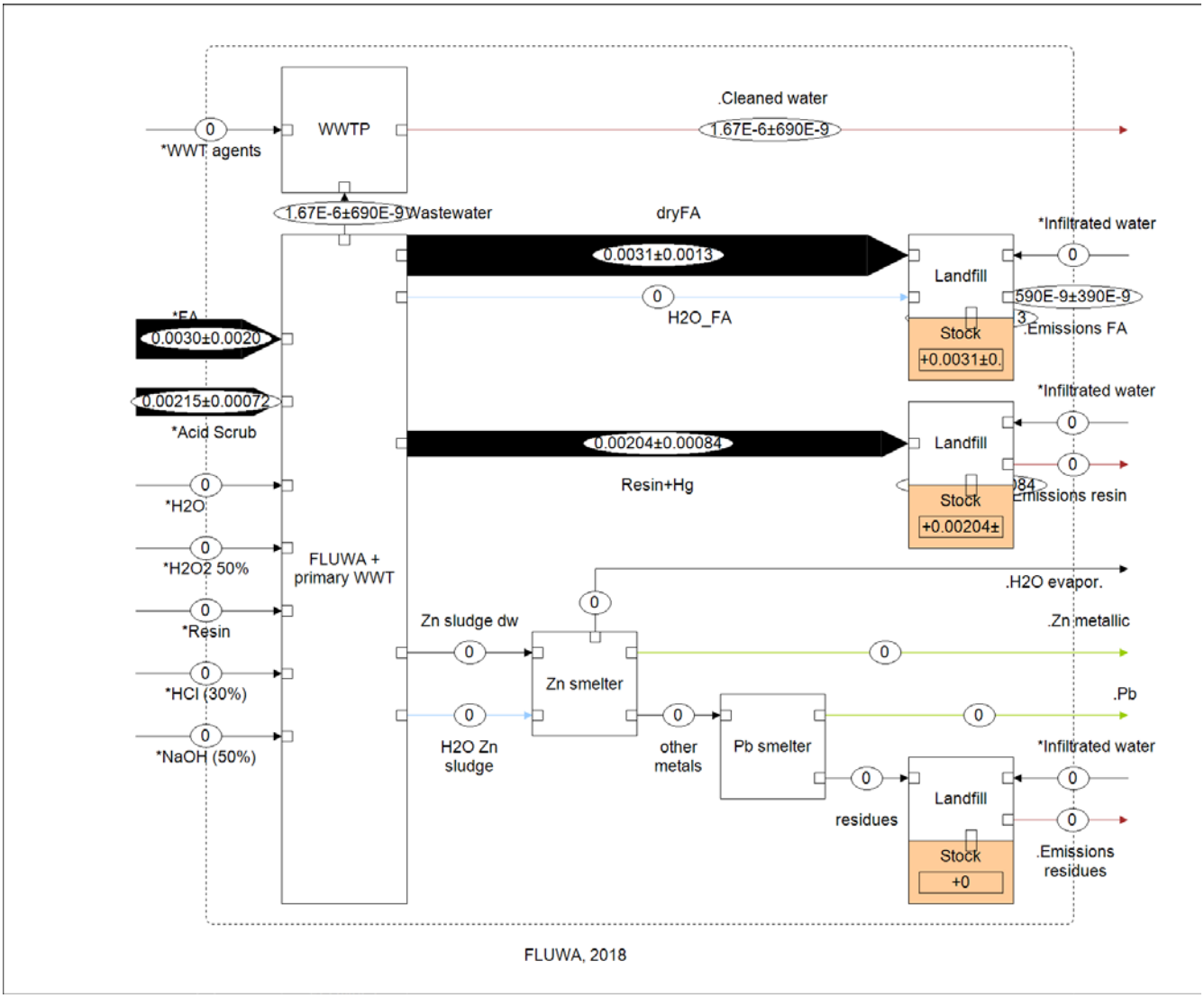


FLUWA, 2018

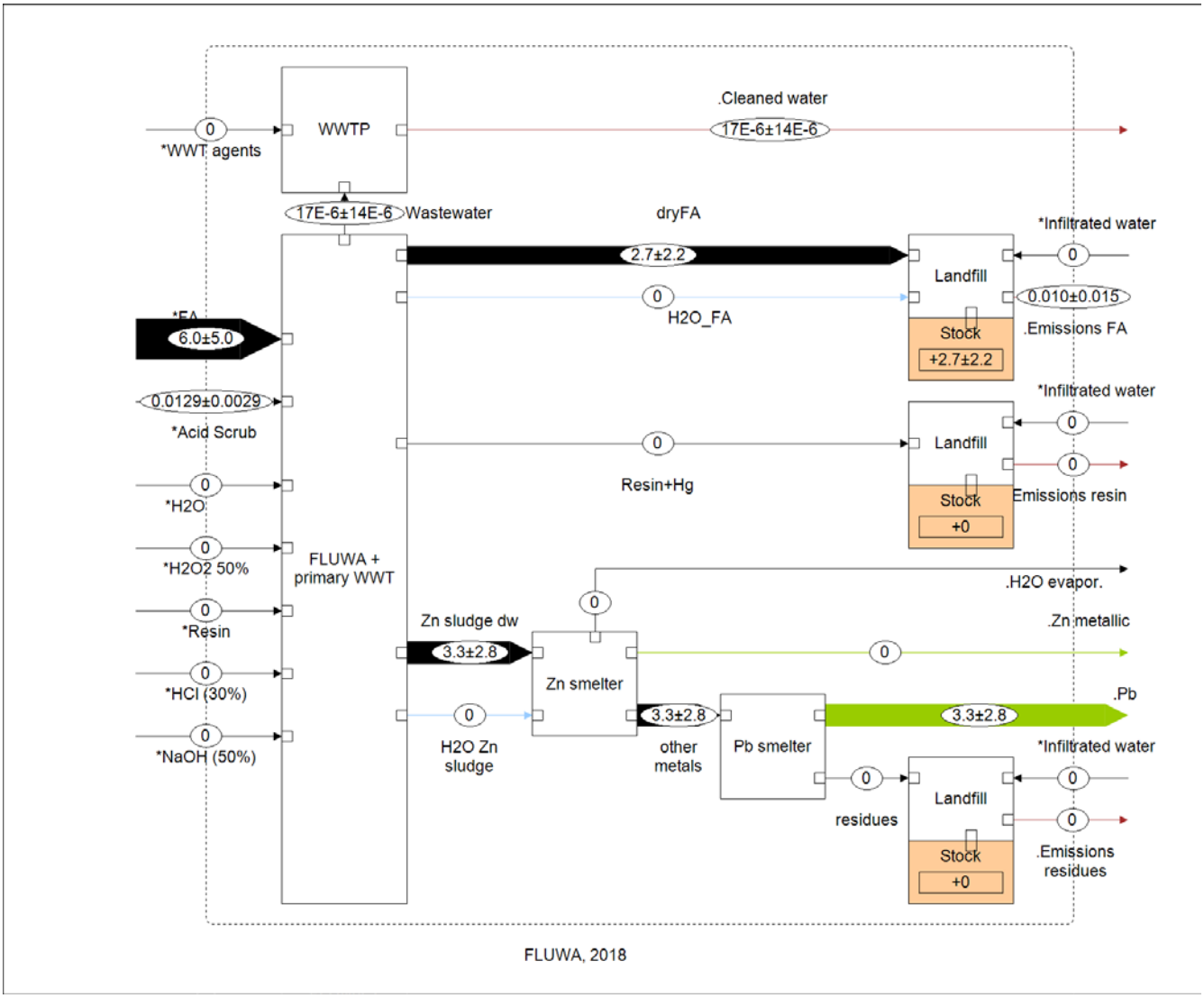
- **Cu (figure below)**



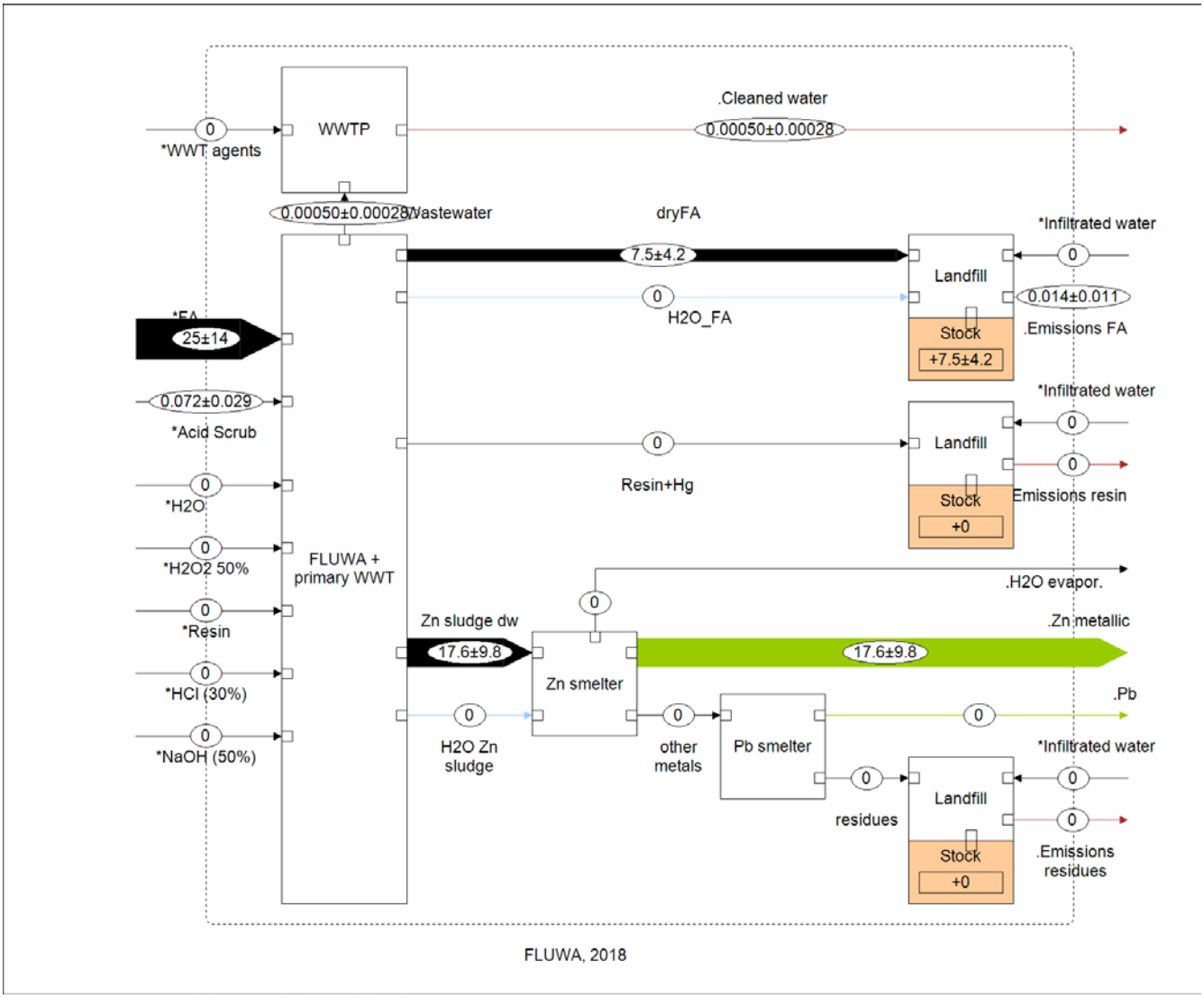
- **Hg (figure below)**



- **Pb (figure below)**

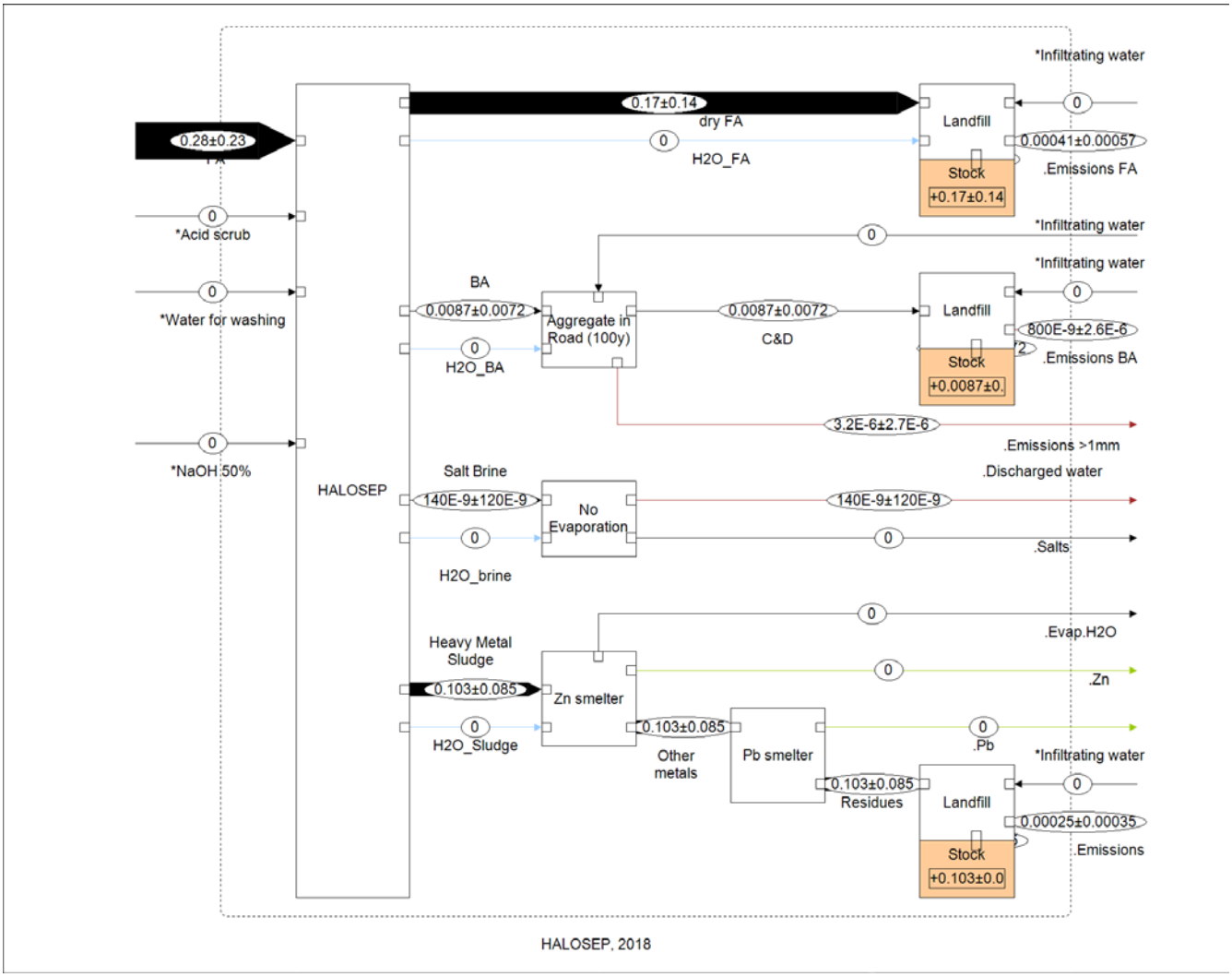


- **Zn (figure below)**

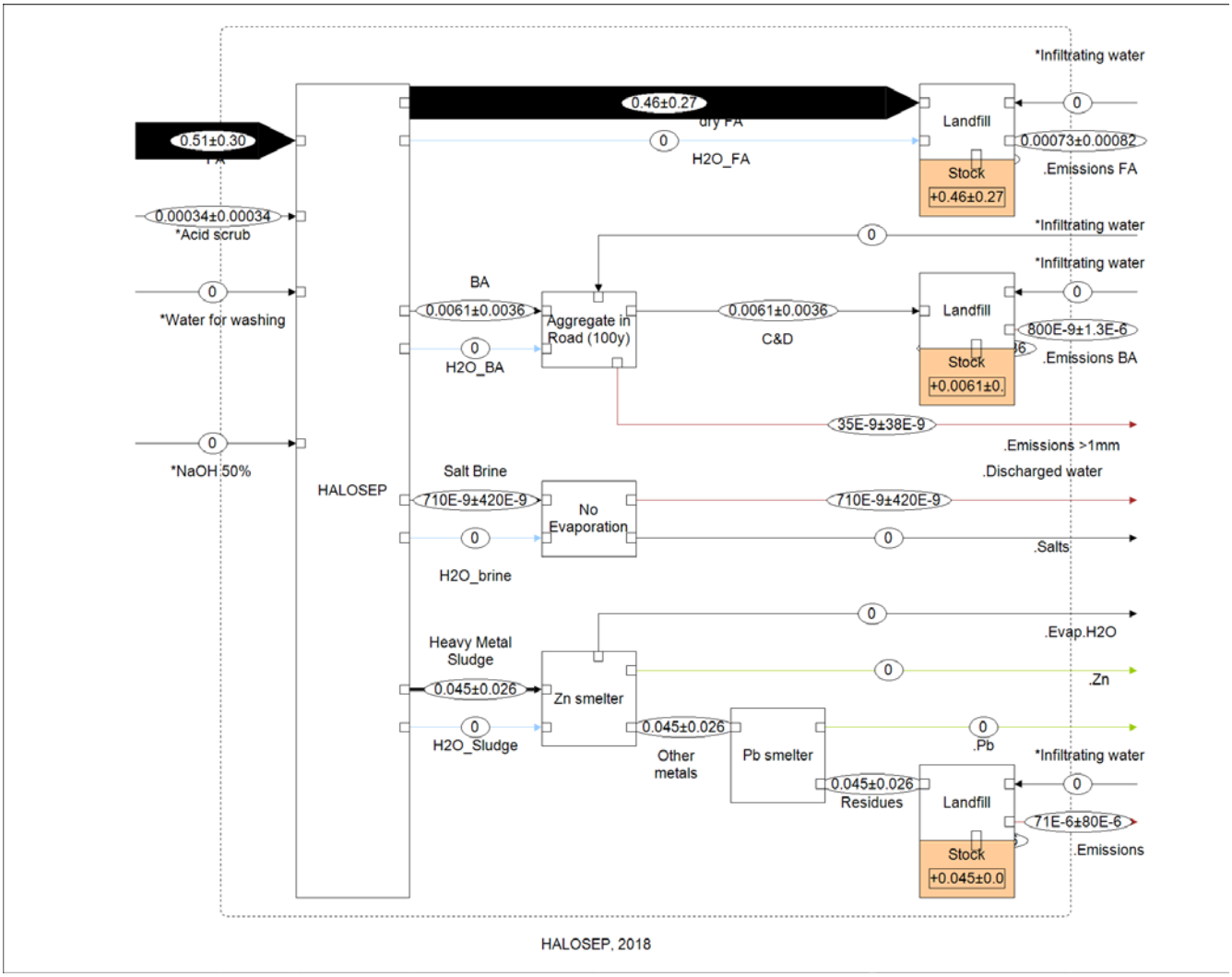


Scenario S5 (Halosep), 500y

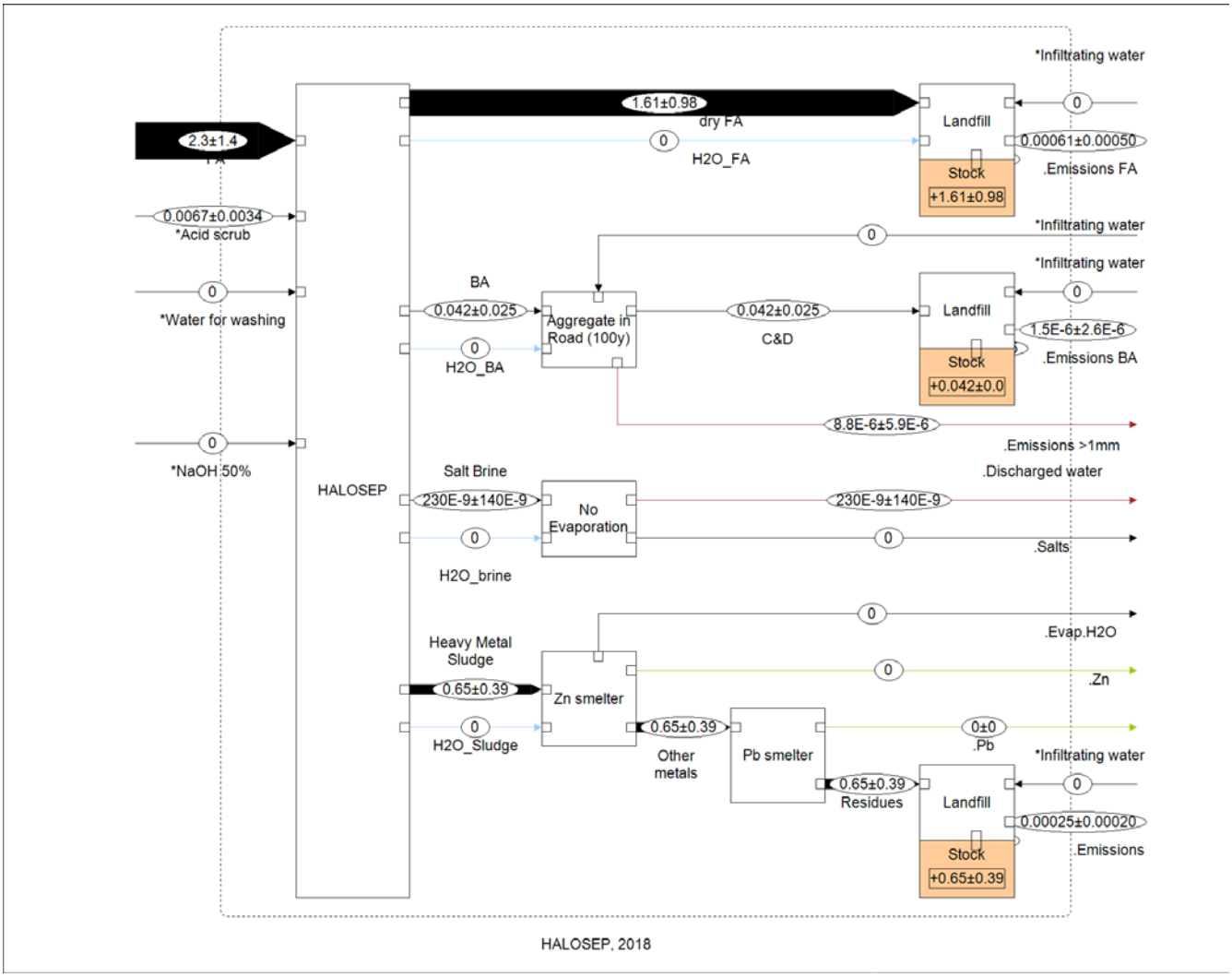
- **As (figure below)**



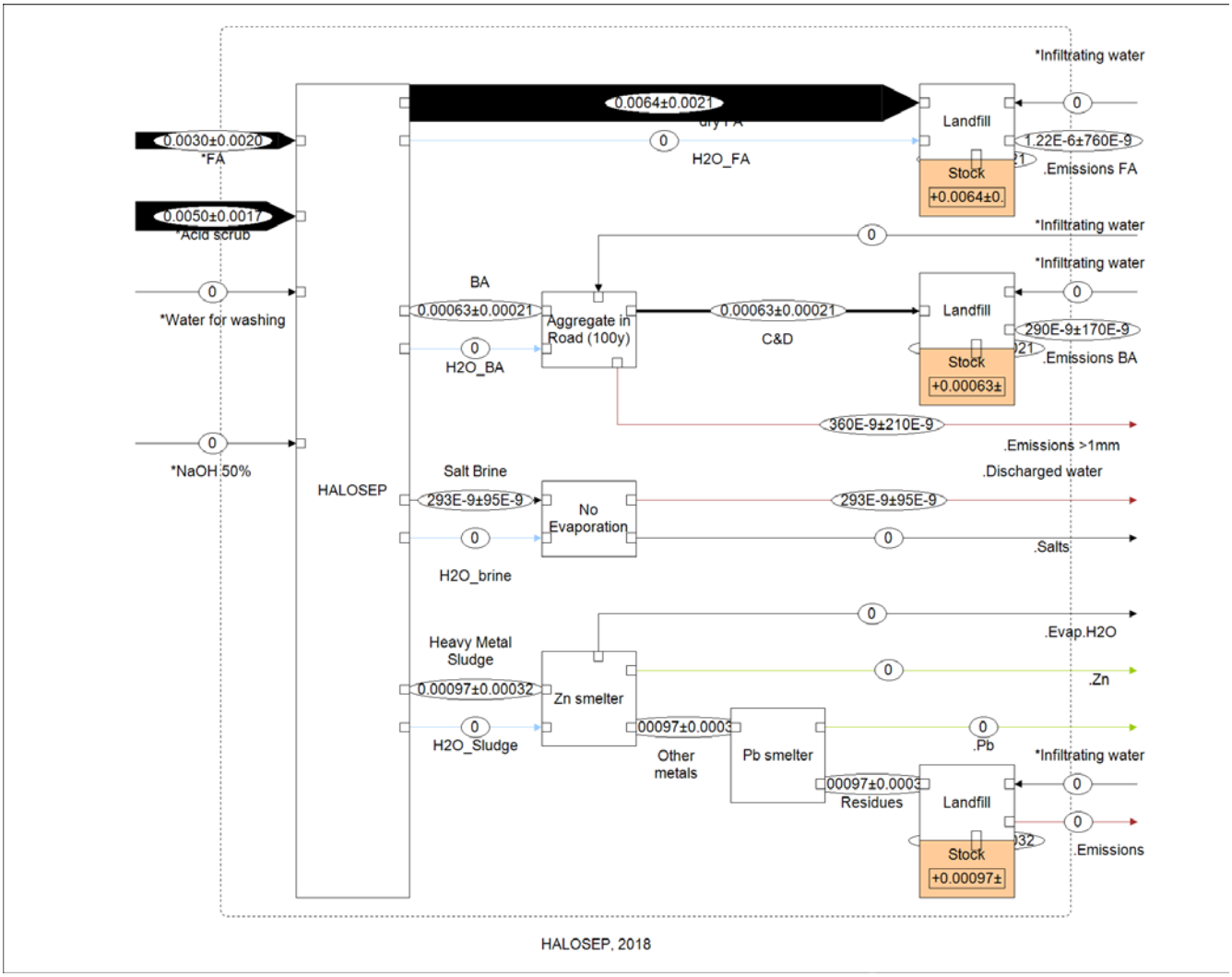
- **Cr (figure below)**



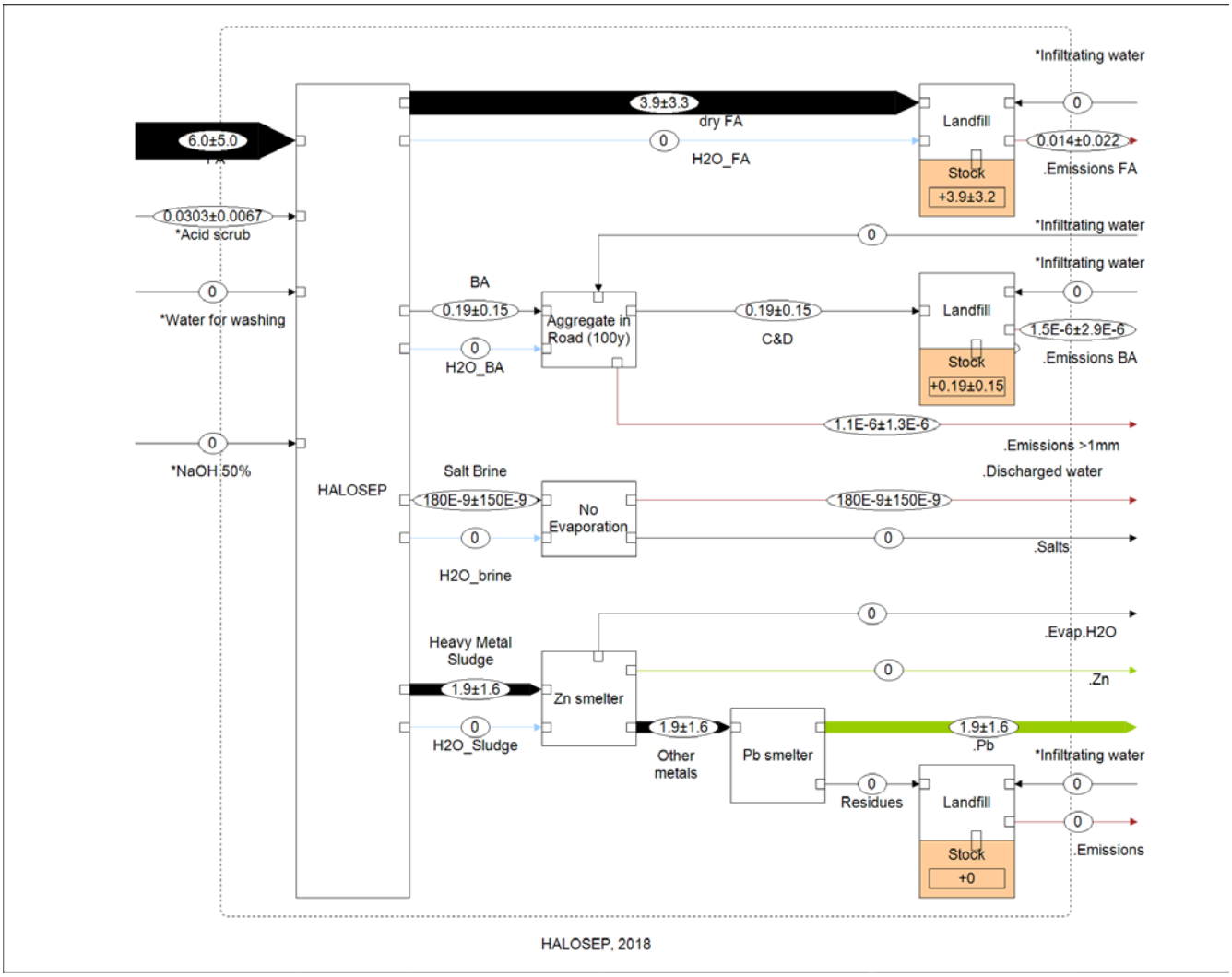
- **Cu (figure below)**



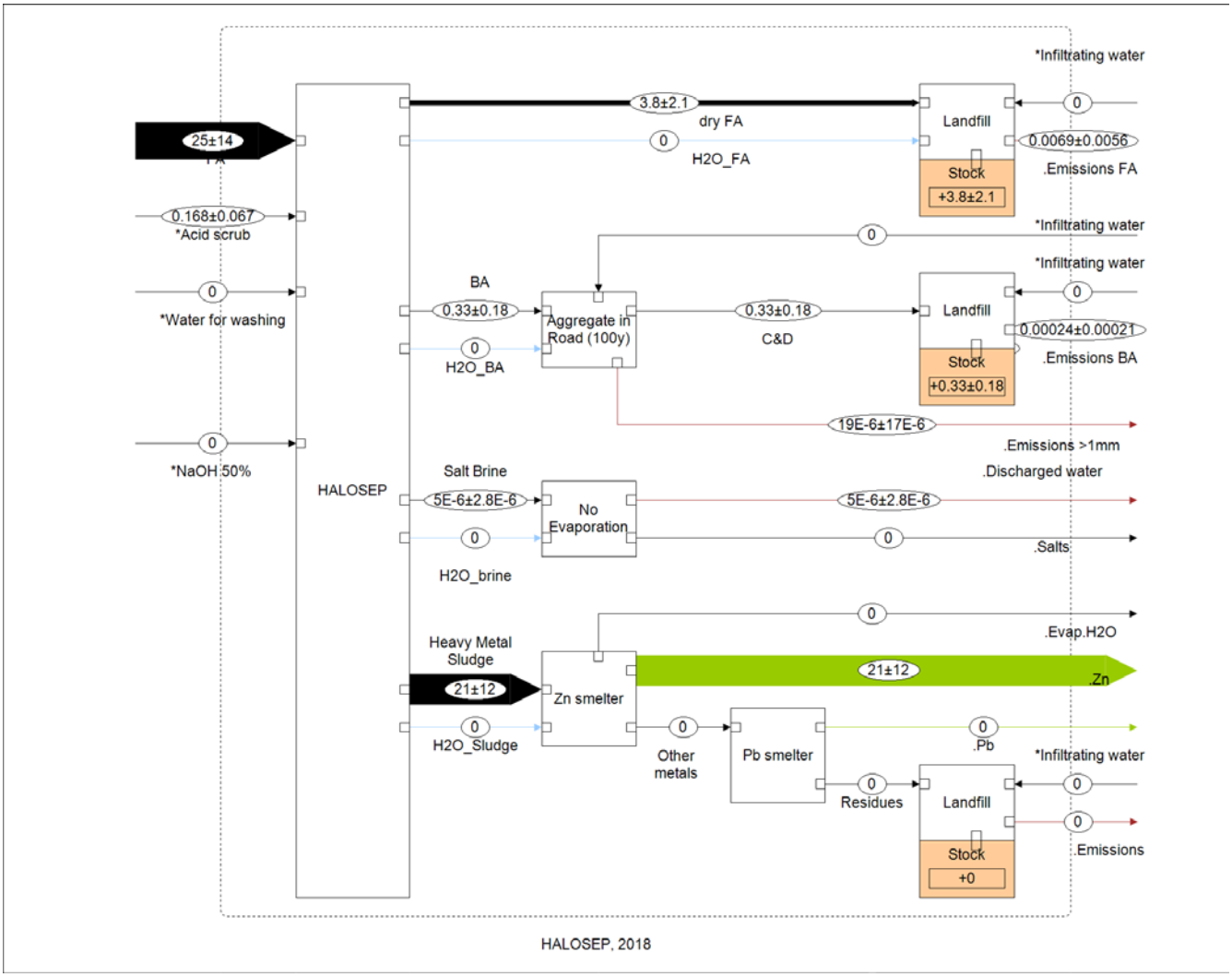
- **Hg (figure below)**



- **Pb (figure below)**

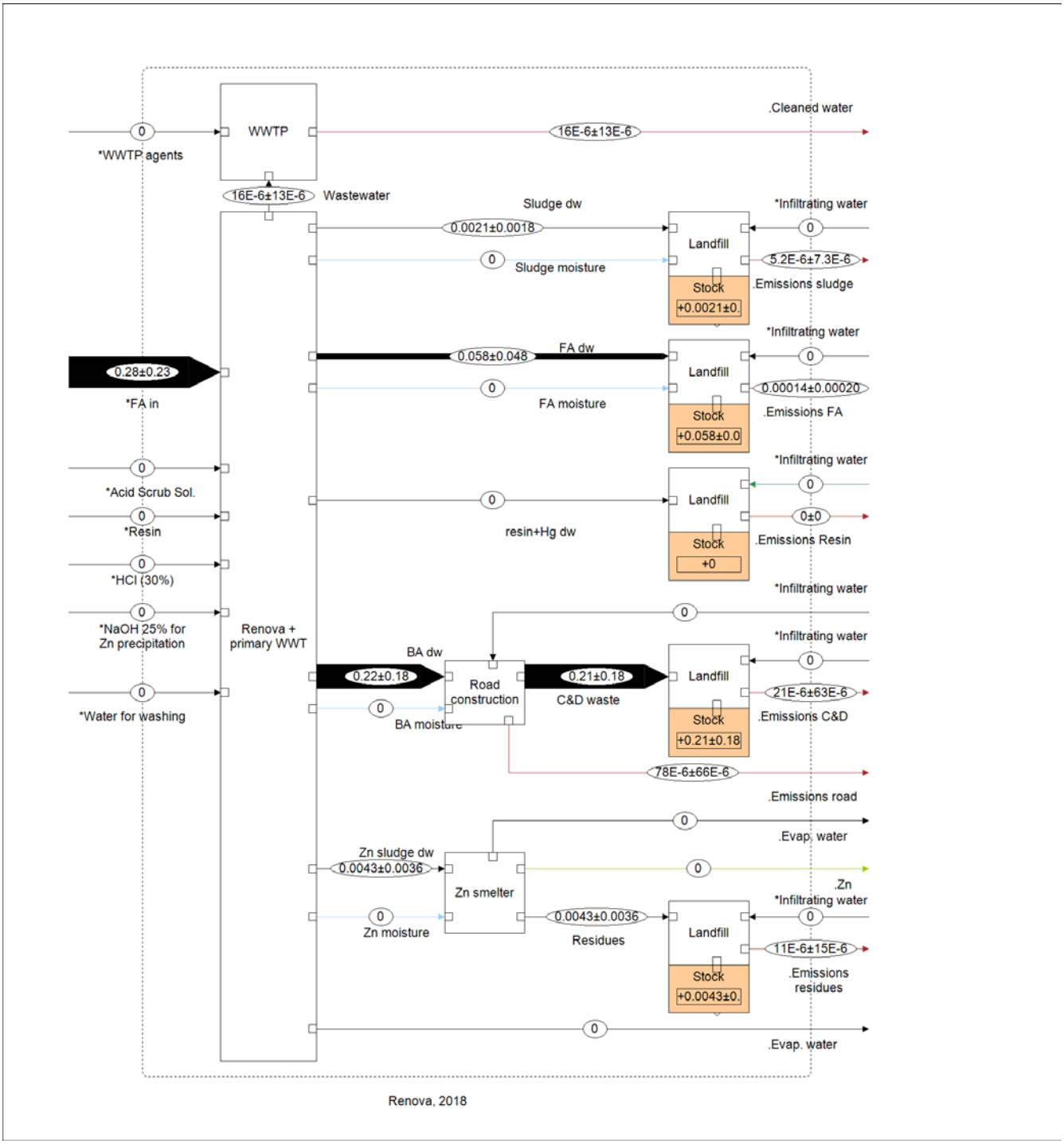


- **Zn (figure below)**

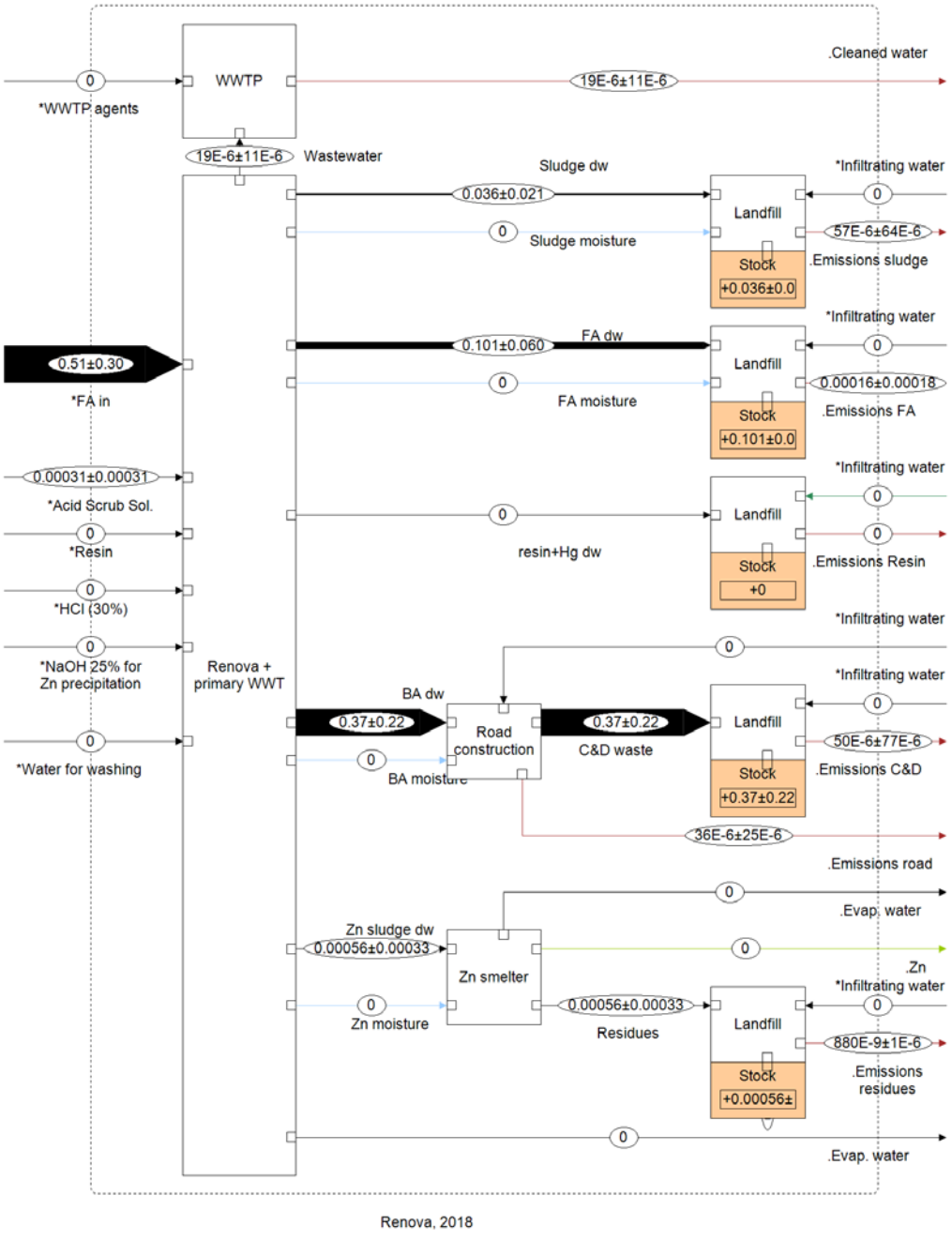


Scenario S6 (Renova), 500y

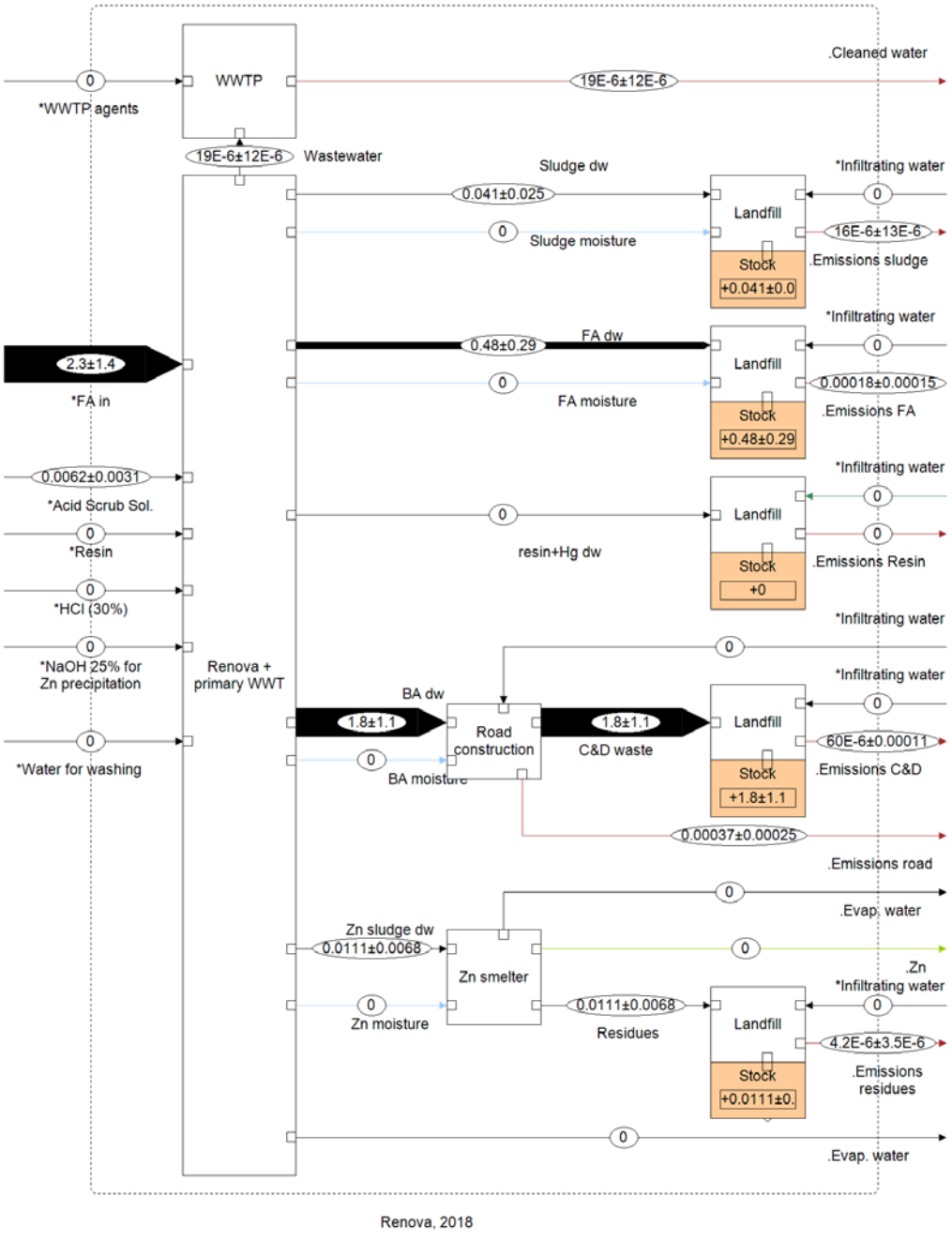
- **As (figure below)**



- **Cr (figure below)**

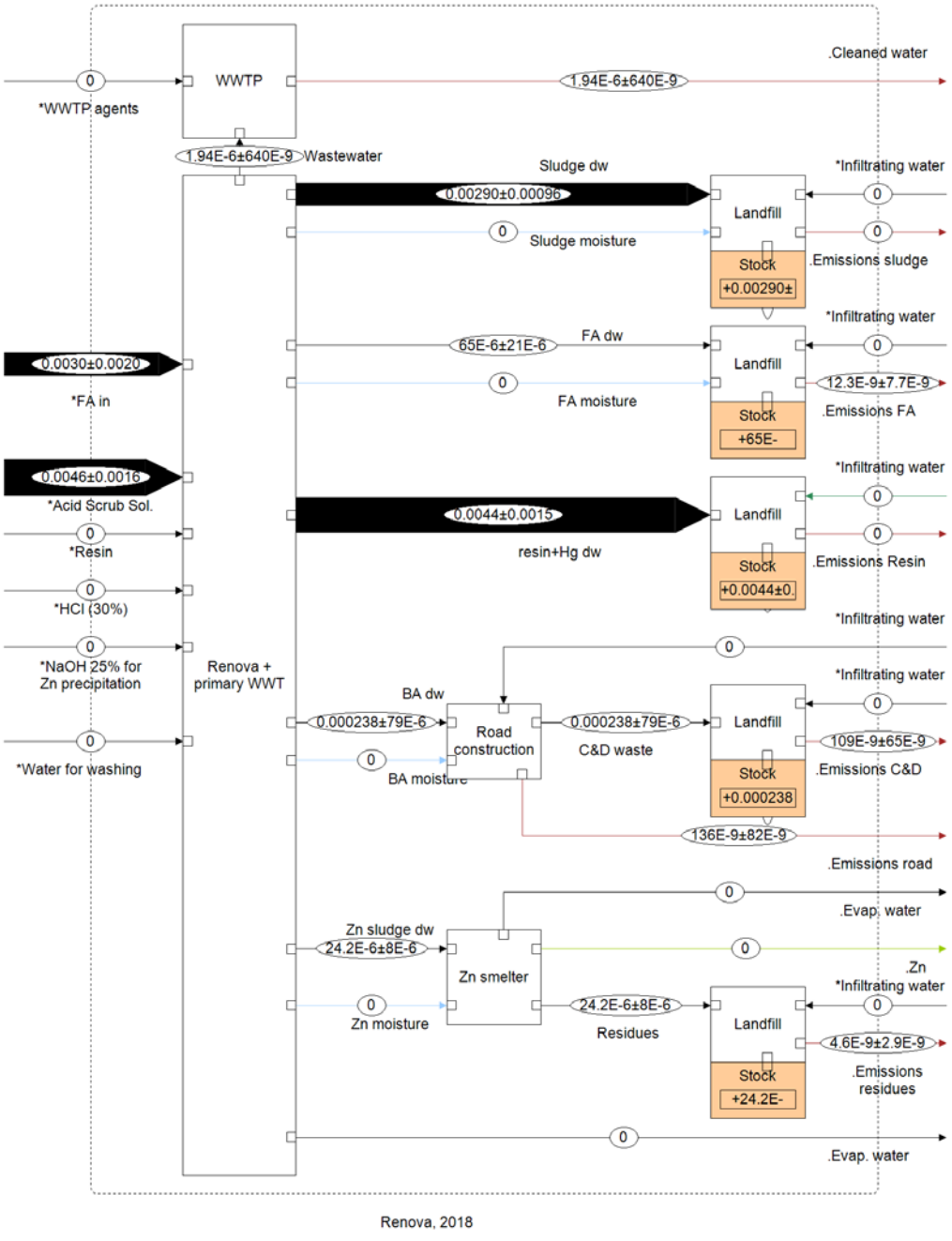


- **Cu (figure below)**

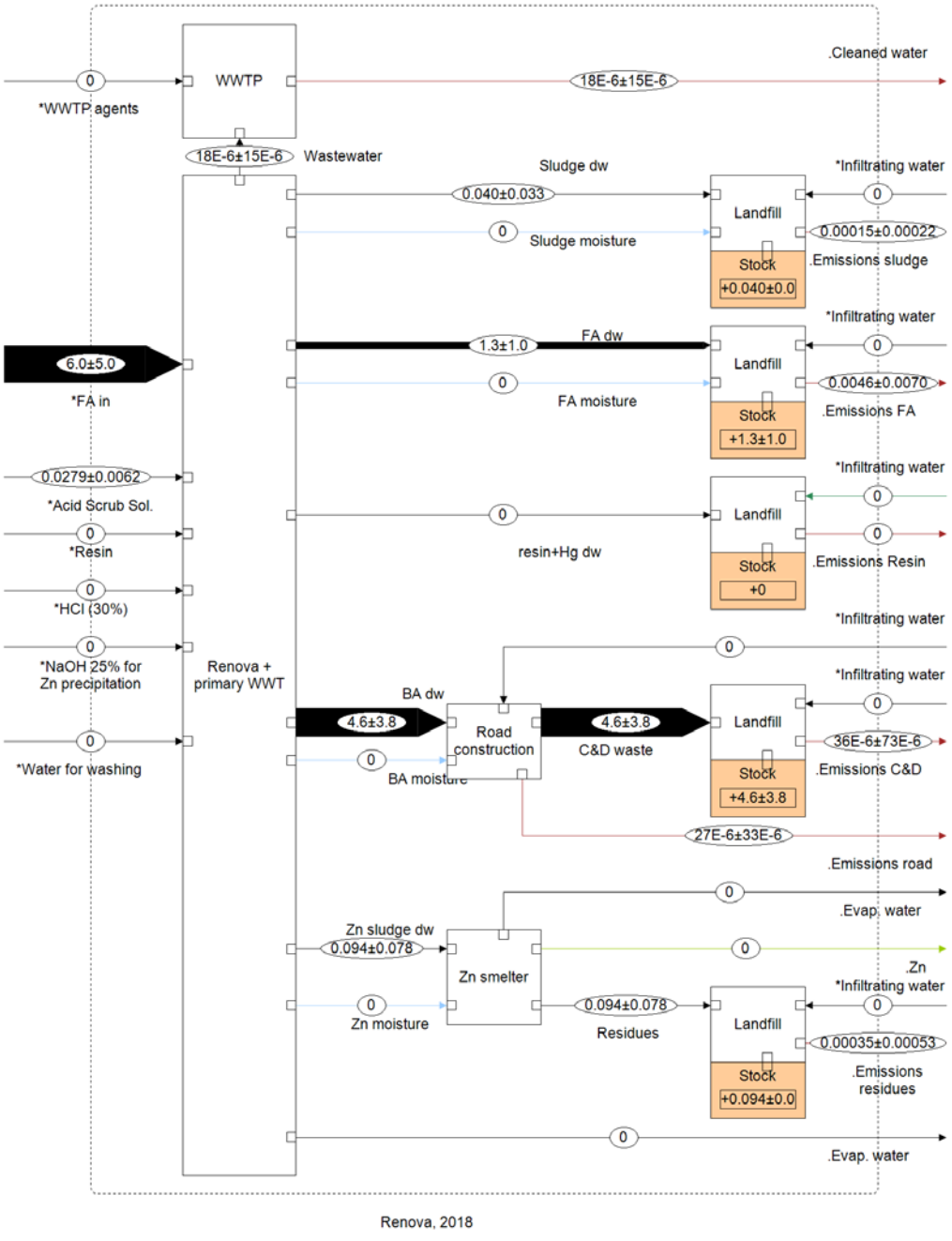


Renova, 2018

- **Hg (figure below)**



- **Pb (figure below)**



- **Zn (figure below)**