Preliminary study of tin slag concrete mixture

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Abstract. The study focuses on practices to facilitate tin smelting industry to reduce radioactive waste product (Tin Slag) by diluting its radioactivity to a safe level and turning it to a safer infrastructural building product. In the process the concrete mix which include Portland cement, sand, tin slag, water and plasticizer are used to produce interlocking brick pavements, piles and other infrastructural products. The mixing method follows DOE (UK) standard method of mixing targeted at in selected compressive strength suitable for its function and durability. A batching machine is used in the mixing and six test cubes are produced for the test. The testing equipment used are a compressional machine, ultrasonic measurement and a Geiger Muller counter to evaluate of the concrete mix to find the lowest emission of radiation surface dose without compromising the strength of concrete mix. The result obtained indicated the radioactivity of tin slag in the mixing process has reduced to background level that is 0.5 µSv/h while the strength and workability of the concrete has not been severely affected. In conclusion, the concrete mix with tin slag has shown the potential it can be turned into a safe beneficial infrastructural product with good strength.

1. The first section in your paper

Malaysia is one of the major world's tin-producing countries. Tin ingot for export is produced from smelting plants. In smelting process, tin ore concentrates which contain significant amount of radioactive minerals such as monazite, zircon and ilmenite were used as raw materials. In the process, cassiterite (SnO2) is reduced to tin metal by heating with carbon at 1200°C to 1300°C. Reverberatory furnaces are used to smelt tin concentrate and to re-smelt slag (the waste left after the ore has been smelted) for additional tin recovery. A furnace charge consists of cassiterite, a carbon reducing agent, and limestone and silica fluxes. The molten batch is tapped into a settler from which the slag overflows into water, where the molten slag is granulated and solidifies to glass-like material[20].

Tin slag contains lime, iron, silica, small amount of heavy metals and natural occurring radioactive materials such as uranium series and thorium series [20][16]. The highest reading, recorded while travelling near monazite and zircon mineral dumps, was 13 times the mean environmental radiation level of in Malaysia. It is evident that the radioactive material dumps on the roadsides can influence...
the radiation level on the road [15]. High background dose rates were detected in area where tin slag is used as sea defense [10].

There are significant needs to be addressed in using tin slag for commercial used indoor or outdoor. Concrete mixture was considered due to its multiple usages as outdoor and indoor or buried products to isolate waste product such as tin slag. The paper reviews some preliminary works on tin slag concrete mixing which is prepared in accordance to DOE method of mixing is in accordance to British Standard.

Tin slag contains elevated concentrations of radionuclides from both the uranium and the thorium decay series and is sometimes used as a source of niobium and tantalum. Table 1 shows the activity concentrations of radionuclides in tin slag according to Omar et al. [16].

Table 1. The activity concentrations of radionuclides in tin slag (Omar, 2008).

| Sample     | $^{238}$U (Bq/g) | $^{226}$Ra (Bq/g) | $^{232}$Th (Bq/g) | $^{228}$Ra (Bq/g) |
|------------|------------------|------------------|------------------|------------------|
| Tin Slag 1 | 3.6              | 2.4              | 5.1              | 1.0              |
| Tin Slag 2 | 6.7              | 3.4              | 7.3              | 1.2              |
| Tin Slag 3 | 0.9              | 0.5              | 0.8              | 1.0              |

The use of slag might need to be restricted, especially in building materials where it could give rise to high indoor radon or thoron concentrations and gamma radiation [17]. Therefore the isolation of tin slag in building material should not be indoor but buried or as infrastructure material. Table 2 shows Ra-226 and Th-232 contents in various building materials.

Table 2. Ra-226 and Th-232 contents in some German building materials and wastes (Winter and Wicke, 1993).

| Material         | $^{226}$Ra (Bq Kg$^{-1}$) | $^{232}$Th (Bq Kg$^{-1}$) |
|------------------|---------------------------|---------------------------|
| Granite          | 30-500                    | 17-311                    |
| Brick            | 10-200                    | 12-200                    |
| Limestone        | 4-41                      | 2-20                      |
| Gypsum           | 2-70                      | 2-100                     |
| Concrete         | 7-92                      | 4-71                      |
| Light-weight concrete | 6-80               | 1-60                      |
| Old copper slag  | 861-2100                  | 18-78                     |
| Tin slag         | 1000-1200                 | 230-340                   |
| Brown coal ash   | 4-200                     | 6-150                     |

Proper management of tin slag are important to ensure the public and environment are safe, current and in the future. Malaysia implemented 1 Bq g$^{-1}$ as the clearance limit for naturally occurring radionuclide from series of uranium and thorium, as stipulated in the Atomic Energy Licensing (Radioactive Waste Management) Regulations 2011. Processing of mineral disposal of waste containing naturally occurring radionuclides below the activity concentration of 1 Bq g$^{-1}$ were exempted from regulatory control (AELR, 2011). Table 1 and 2 show that total activity concentration in tin slag always higher than 1 Bq g$^{-1}$. Because most of tin slag containing higher activity concentration than the clearance limit, processing and disposal of tin slag need approval by the Atomic Energy Licensing Board (AELB). From the table 2 building material shows tin slag give Radium 226 a concentration of 1–1.2 Bq g$^{-1}$. Thorium 232 of 0.23–0.34 Bq g$^{-1}$. The annual limit public dose is 1 mSv. This 1mSv/year is equal to 0.11 µSv/hr. Public exposure is subjective to time of occupancy and distance from radiation source. The net public dose must not above annul limit. Since the concrete is
exposed or embedded to the infrastructure. The exposure is calculated from occupancy factor of 0.8 for indoor and 0.2 for outdoor [18].

2. Methodology
Concrete mixing procedure BRE Mix Design Method [8] (formerly known as DoE method of mixing) which is in accordance to British Standard is adopted in this work. Basically it is a weight proportion method where all its constituents are measure by weighing with the electric mass balance. All the concrete mixtures, which are, coarse aggregates, fine aggregates, cement and water is placed in the batching machine. The concrete mixture is tested for slump before making cubes for strength test. There are three types of concrete mixtures. They are as follows normal concrete M30, 100% tin slag replacing sand and 20% tin slag replacing sand. Table 3 shows the mix proportion used in the experiment.

Table 3. The mix proportion (* Cube volume 0.01 m$^3$).

| Mix       | Proportion      | W/C | Cement (kg) | Fine aggregates | Coarse aggregates |
|-----------|-----------------|-----|-------------|-----------------|------------------|
| Normal concrete M30 | 1:0.5:2.7:1.48 | 0.5 | 5.04        | 13.8            | 0                |
| 100% slag M30          | 1:0.54:2.17:2.4 | 0.54| 3.62        | 0               | 7.85             |
| 20 % slag M30           | 1:0.5:1.8:2.32 | 0.5 | 4.2         | 6.36            | 1.59             |

Material type and grade used are portland cement grade 43, fine aggregates (River sand) of 600µ sieve passes 22%, clean water with cement to water ratio, tin slag granular with particle 600µ sieve passes 11%, coarse aggregates (granite) of 20 mm diameter. Mix design process in this experiment, for the mix design process the following factors have to been taken into consideration are minimum compressive strength required, water to cement ratio, type of cement, durability, workability and water content, choice of aggregate, cement content and aggregate content.

The concrete containing tin slag cubes were prepared based on British DOE method sample preparation (BS 1881: part 108, 1983). The block sizes were 150mm x 150mm x 150mm and the workability is medium. The samples were cured by immersion into water for 28 days. The samples were tested at the age of 7 days, 14 days and 28 days. Testing procedure for destructive and non-destructive testing is shown in table 4 below.

Table 4. List of tests.

| Destructive testing          | Non-destructive testing                                      |
|------------------------------|-------------------------------------------------------------|
| Compression cube test        | Sieve testing of sand for 600 µ                             |
|                              | Slump test                                                  |
|                              | Weight test                                                 |
| ultrasonic pulse velocity (UPV) testing |                                              |
| Surface radiation dose test (MS EN 12504-4: 2013) |
A dual dial gauge hydraulic compression machine is used for compression cube test in accordance to BS 1881 Part: 116, 1983. Firstly the cube is chosen with flat surfaces and is placed against the machine contact surface at the centroid. The dial marker is set to zero with the dial gauge. The compression machine is loaded by lowering its load cell. The marker will indicate its result as the compression decreases or reaches its peak.

The slump test equipment is shown in figure 1 and procedure in accordance to BS1881 Part: 102, [2]. The mix concrete is placed in the cone (bottom diameter is bigger) in three layers and 25 times the steel rod is stamped in every layer to the top of the cone. The cone is pull up and the slump is measured by putting the cone beside the concrete mass and rod is placed perpendicular to the top surface. The gap between the concrete mass and the rod is the slump measurement.

![Figure 1. Test apparatus for concrete workability.](image)

The UPV test instrument used is TICO as shown in figure 2 (a) and (b) or PUNDIT or their equivalent company approved instrument in accordance to BS 1881 part: 203, 1986. The probes shall be in general selected from PUNDIT or equivalent with frequency about 50kHz Calibration Block or reference bar as provided by the equipment manufacturer with known and calibrated transit time. Conventional couplant – typical couplants are petroleum jelly, grease, soft soap and kaolin/glycerol paste. No couplant is required for exponential tip probe. Surface transmission should be only used in cases i) when one face of the concrete is accessible, ii) when the depth of a surface crack is to be determined or iii) when the quality of the surface concrete relative to the overall quality is of interest.

### Table 5. The general quality of concrete based on UPV (Malhotra V.M, 1975)

| Pulse velocity (m/s) | Quality      |
|---------------------|--------------|
| Above 4500          | Excellent    |
| 3600 – 4500         | Generally good|
| 3000 – 3600         | Questionable |
| 2100 – 3000         | Generally poor|
| below 2100          | Very poor    |
Common usage is in the determination of the variability and quality of concrete and in the estimation of crack depth. Using a variety of transmission techniques, the extent of such defects such as voids, honeycombing, cracks and segregation can be determined. The method can also be used in the integrity testing of repairs and construction joints, particularly in water retaining structures. This technique is also useful when examining fire damaged concrete. It may also be used to detect presence and degree of microcracking in steel. Transducers of different frequencies are needed for different types of materials. Ultrasonic pulse velocity is the most recommended NDT used for assessing concrete strength (Malhotra, 1975).

The equipment used is a Geiger Muller counter as shown in figure 2 (b). The procedure is based on MS EN 12504-4: 2013. The surface radiation levels were measured in unit μSv/hr. Each surface of the cubic sample was measured with the counter and the average value is calculated.

3. Results and Discussion

The main purpose of this experiment is to find the lowest emission of radiation surface dose rate in modified tin slag concrete mixture without compromising strength of concrete. The first information of the mineral contain in tin slag was measured which obtain from Malaysian Smelting Corporation Berhad. It was analyzed using neutron activation analysis and the result shown in table 6 with the Certificate reference number NAA/4D/17 (23).

Based on UPV result, the general condition of concrete mixture type is graded excellent as shown in table 7. It can be seen that concrete mixture with 20% tin slag has highest velocity value compared to concrete mixture with 100% tin slag within 7 – 14 days but similar in strength. Meanwhile, both concrete mixtures have shared the same value of velocity and strength after 28 days.

During the curing stage concrete strength generation shows increment of strength for 7 days and gradually low generation for 14 days and achieved higher strength at 28 days shown in table 7. Results of the experiment are tabulated in table 8. It is found that the concrete density and slump (workability) are increased with the introduction of tin slag in the mix. However, the radiation level is also increased slightly when the tin slag is introduced.
Table 6. Elements Analysis in tin slag sample.

| No. | Element | Slag MSC – 1 (Concentration) | Slag MSC – 1 (Concentration) |
|-----|---------|------------------------------|------------------------------|
| 1.  | Sm      | 414 µg/g                     | 401 µg/g                     |
| 2.  | U       | 116 µg/g                     | 115 µg/g                     |
| 3.  | Yb      | 127 µg/g                     | 121 µg/g                     |
| 4.  | As      | 162 µg/g                     | 43.8 µg/g                    |
| 5.  | Sb      | 3.2 µg/g                     | 3.3 µg/g                     |
| 6.  | Br      | <0.5 µg/g                    | 5.0 µg/g                     |
| 7.  | La      | 0.29 %                       | 0.27 %                       |
| 8.  | Ce      | 0.44 %                       | 0.43 %                       |
| 9.  | Lu      | 11.8 µg/g                    | 11.1 µg/g                    |
| 10. | Th      | 0.13 %                       | 0.13 %                       |
| 11. | Cr      | 0.18 %                       | 0.18 %                       |
| 12. | Hf      | 370 µg/g                     | 358 µg/g                     |
| 13. | Ba      | 0.46 %                       | 0.38 %                       |
| 14. | Nd      | 0.14 %                       | 0.13 %                       |
| 15. | Cs      | 9.9 µg/g                     | 15.2 µg/g                    |
| 16. | Tb      | 31.4 µg/g                    | 29.2 µg/g                    |
| 17. | Sc      | 102 µg/g                     | 94.8 µg/g                    |
| 18. | Rb      | 419 µg/g                     | 292 µg/g                     |
| 19. | Fe      | 12.40 %                      | 12.42 %                      |
| 20. | Zn      | 0.26 %                       | 0.22 %                       |
| 21. | Co      | 24.7 µg/g                    | 27.5 µg/g                    |
| 22. | Eu      | 9.5 µg/g                     | 9.6 µg/g                     |

Table 7. Results experiment of UPV.

| Concrete Mixture type | concrete cube age in pulse velocity (m/s) | Strength |
|-----------------------|-------------------------------------------|----------|
|                       | 7 days | 14 days | 28 days |               |
| 20 % slag             | 5430   | 5554    | 5610    | Excellent     |
| 100 % slag            | 5332   | 5497    | 5610    | Excellent     |
| Normal M30 concrete    | 5340   | 5408    | 5508    | Excellent     |

Table 8. Results of the experiment.

| Concrete Mixture type | Density kg/m³ | Concrete grade | 600µ sieve | Radiation µSv/hr | Slump (mm) | Ultrasonic pulse velocity (m/s) | Compressive test at 28 days (N/mm²) |
|-----------------------|---------------|----------------|-------------|------------------|------------|---------------------------------|-----------------------------------|
| Normal                | 2.192         | M30            | 22%         | 0.5              | 10         | 5508                            | 20.0                              |
| 20% tin slag          | 2.488         | M30            | 24%         | 0.8              | 20         | 5610                            | 24.8                              |
| 100% tin slag         | 2.488         | M30            | 11%         | 1.5              | 25         | 5610                            | 20.8                              |
The test result in table 8 shows the increase of density with percentage of tin slag. The 20% tin slag mixture gives the best result with 0.8 µSv/hr surface dose and 24.8 N/mm² in strength. The compressive strength is good for 7 days. This shows good early strength formation. In overall the 20% tin slag shows surface radiation below dose limit 1 µSv/hr and 100% tin slag above the s.. In short, it indicates that percentage of tin slag is slightly effect the concrete strength mixture.

The surface radiation dose 0.8µSv/hr was obtained from 20% tin slag mixture compared with background dose of normal natural occurring radiation material in concrete 0.5µSv/hr. Therefore the net surface radiation is:

\[
0.8\mu\text{Sv/hr} - 0.5\mu\text{Sv/hr} = 0.3 \mu\text{Sv/hr}
\]  

Total limit dose 0.3µSv/hr x 0.2 (occupancy factor) x 24 (hr/day) x 365 (day/year)  
\[= 525 \mu\text{Sv/year} \] (1)

Therefore surface dose limit of 0.525mSv/year is less than 1 mSv/year which is the annual limit for public member. The result suggest 30% and 40% of tin slag mixture may be used as long as the public dose limit for radiation is not breach and the concrete strength is maintain.

4. Conclusion
The factor effecting surface radiation is tin slag percentage in the concrete mixture. The isolation of tin slag is suc-cessful in concrete mixture with 20% sand replacement formulation which only emits the best result of 0.8 µSv/hr surface dose. Where net total limit dose of 525 µSv/year is about 50% lower than 1 mSv/year annual limit dose for public exposure for tin slag concrete mixture and 20% tin slag mixture give the best strength development for 28 days as 24.8 N/mm². Preliminary result conclude that tin slag additional is considered able to suit in concrete envi-ronment and replaced sand in normal concrete at optimum ratio of 20%.

5. Further works
The future work in this project explores the new mix design for outdoor application such as a cement brick mortar for brick laying, pole for agricultural or livestock fencing in rural areas project in helping the rural communities and underground civil foundation structure. The research includes studies on new mix designs that would enable the incorporation of the idea of altering water-cement ratio mixture for better improvement.

The facts that tin slag has a high density composition makes it possible for making bricks or wall that can be used as a radiation shielding. The tin slag collected from tin smelting industry tested with NAA method (table 6) has shown to contain twenty two elements. However, to reduce the effect of radiation some elements may be removed by special extraction processes.

The amount of the tin slag used in these mix design is less compared to the tin slag waste from the tin smelting industry found in Malaysia. The waste, in large amount, is threatening to the environment due to the fact that it needs much bigger area for safe dumping purpose in safe manner. Typically in tin smelting industry the sighting of piling up waste is common. This is not healthy for long term exposure to human being as the small particles from the tin slag may be inhaled into the body. It is much more crucial since some of the particles are radioactive. Hopefully, through this project as a start some proposals will be given due attention and the appropriate actions may be carried out accordingly in the next task of plan. Thus this would pave much more interesting and beneficial code of conduct and practices as the Nuclear Malaysia and local government struggle to find ways and procedures to solve the pile of tin slag.

6. References
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