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Comparison of radioactive transmission and mechanical properties of Portland cement and a modified cement with trommel sieve waste

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Abstract

In this study, it was aimed to stabilize trommel sieve waste (TSW) occurring during manufacture of borax from tincal. The effects of TSW added on the mechanical properties and radioactive transmission of modified cement prepared by adding TSW to clinker was investigated. The properties which TSW as additive caused the cement to gain were tested and compared with normal Portland cement.

Measurements have been made to determine variation of mass attenuation coefficients of TSW and cement by using an extremely narrow-collimated-beam transmission method in the energy range 15.746–40.930 keV with X-ray transmission method. The characteristic Kα and Kβ X-rays of the different elements (Zr, Mo, Ag, In, Sb, Ba and Pr) passed through TSW and cement were detected with a high-resolution Si(Li) detector. Results are presented and discussed in this paper.

Keywords: Boron wastes; Cement; Waste management; Radioactive transmission; Waste stabilization

1. Introduction

Turkey has the largest boron deposit in the world and about 60% of the world's boron ores are in Turkey. The average boron ores production of Turkey is about 1.3 billion tons per year. The most important boron ores in Turkey are colemanite, ulexite and tincal. Borax from tincal ore is produced by batch process. Production method can be described briefly as: The concentrate tincal ore having about 10-mm particle size is fed to a stirred reactor containing water heated to 95–100 °C and dissolves in it. After the treatment, undissolved part of the tinkal ore, called as the trommel sieve waste (TSW), is discharged. For one tone borax production, 500 kg of TSW is obtained and it contains 5.20% B_2O_3 [1]. The amount of this waste is about 250,000 tons/year. The TSW contains some water-soluble and insoluble boron minerals with clay. Boron compounds in this waste discharged to land are dissolved by rainwater, and pass to soil where they form some complexes with heavy metals such as Pb, Cu, Co, Ni, Cd, etc., so that the potential toxicity of these metals increases, and cause some serious health and environmental problems when the complexes pass to groundwater [2].

The researches show that 50% energy reduction during the clinker grinding, development of strength, decreasing in heating temperature of clinker and high resistance against nuclear radiation are the main characteristics of the concrete produced from cement containing borate [3]. In some studies on the removal of solid boron wastes, the recovery of boron from boron wastes or the stabilization of boron wastes with cement, lime and sand has been studied [3–9]. In addition, TSW and other boron wastes are the important industrial wastes taking place during the production of boron compounds. There have been some reports on the

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Table 1
The chemical analyses of TSW and cement

Parameters	Portland cement	Original TSW
B_2O_3, %	–	6.980
SiO_2, %	19.580	14.270
SO_3, %	3.000	0.540
CaO, %	55.400	17.040
MgO, %	3.380	16.270
Fe_2O_3, %	3.000	0.180
Al_2O_3, %	4.880	1.480
Na_2O, %	–	3.840
SrO, %	–	1.000
As_2O_3, %	–	0.004

utilization of these wastes for making cementitious binders and building elements [3,4]. To reduce pollution and disposal of this waste, there is an urgent need to develop useful building materials from them. With this view, investigations were undertaken to produce cementitious binders by blending the TSW with Portland cement as well as by suitably proportioning TSW [6]. In some studies on the removal of solid boron wastes, the recovery of boron from boron wastes or the stabilization of boron wastes with cement, lime and sand has been studied [10,11].

The boration of nuclear reactor coolant for reactor shutdown and during the cool down operation of reactor coolant for refuelling is a routine practice. Liquid radioactive wastes are originated from boric acid control system for safe operation of nuclear power reactors [12]. Thinner or more effective shields can be achieved using cement with dense aggregates such as magnetite, ilmenite, limonite and hematite for attenuation of neutrons and gamma rays. Boron carbide and other boron compounds are widely used as a shielding material, either alone or combined with other materials for radiation shielding [13].

Present study aims essentially to use TSW to prepare a cementitious/composite material which will be able to utilize in different applications such as the constructions, decoration process and radiation attenuation shields. Measurements have been carried out to investigate the mechanical, physical and radiation attenuation properties for cement and TSW.

2. Materials and methods

The materials used in the study were collected from Eti Holding Borax and Acid Factories in Bandırma Turkey. TSW was taken from the outlet of the reactor in which tincal dissolved. This dumpy waste was dried in the air and then it was crushed and ground by mechanical ways. The particle sizes of TSW were not taken into account since it has a crushable structure and completely sieved in a 100-mesh sieve. In addition to this sample, a second TSW sample was prepared using TSW dried 105 °C by the same way of above. Cement and modular sand used in the experiments were provided from Erçimsan-Aşkale Cement Factory in Erzurum, Turkey. Some physical and chemical features of TSW and cement used in the research are presented in Table 1.

A three-cell mold (4×4×12 cm), in dimensions was used to prepare the samples for testing. Clinker, waste, sand and water were well mixed and the mortar obtained was compressed according to the standards and put into the molds and vibrated in a mechanical vibrator. After the top surface of the mold was smoothened by an steel plate, the

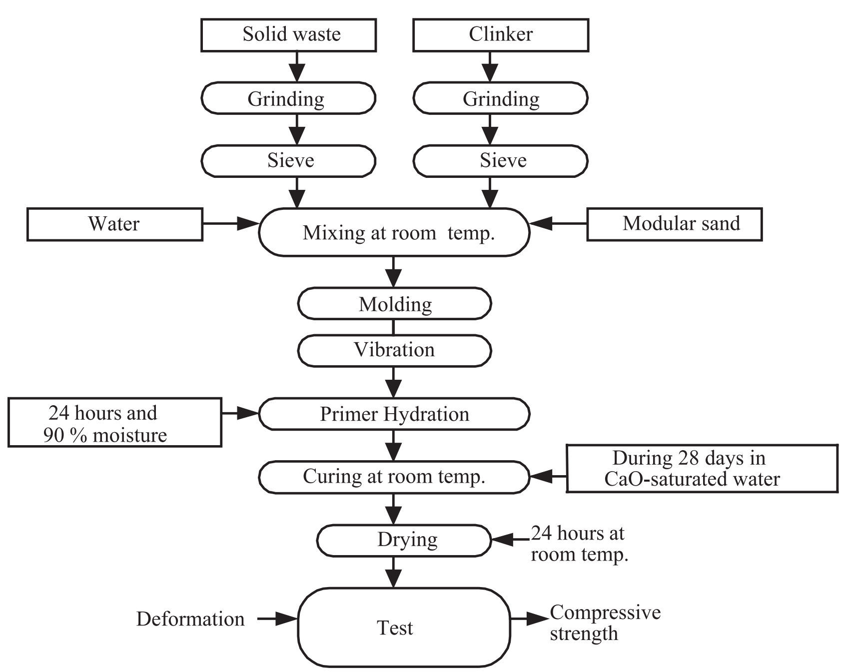

Fig. 1. Flow diagram of cement with TSW production.

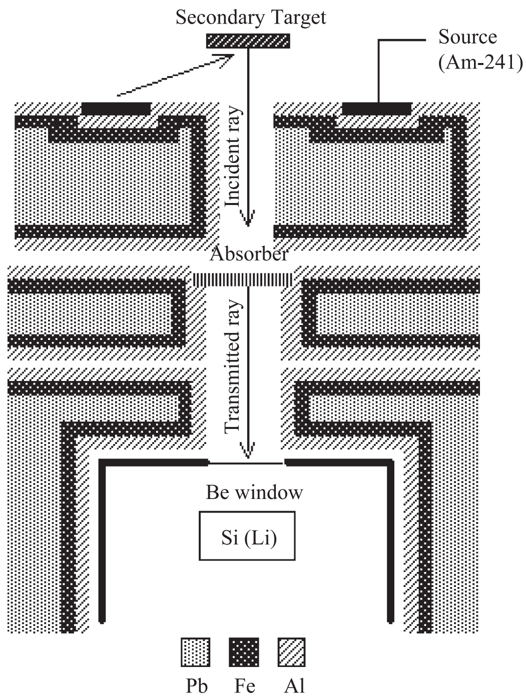

Fig. 2. Schematic diagram of the experimental arrangement for mass attenuation coefficients.

sample was left for the first hydration. In order to reduce the loss of moisture in the samples, the mold was covered with a polyethylene film and kept for 24 h for the first hydration at 20–25 °C and in 90% water-saturated air medium. Then, remolded samples were left in lime-saturated water for 28 days and dried in air. The surfaces of the dried samples were smoothened by carburondum and a compass-measured surface areas and a precision balance determined its weight. After this procedure, compressive strengths, unit weights and other mechanical properties were tested and recorded. The procedure is shown schematically in Fig. 1. The compressive strengths were measured in an universal test equipment, which has a maximum capacity of 10,000 kg/cm^2 by crushing them with automatic loading. Standard methods were employed both in the preparation of the mixtures and the measure-

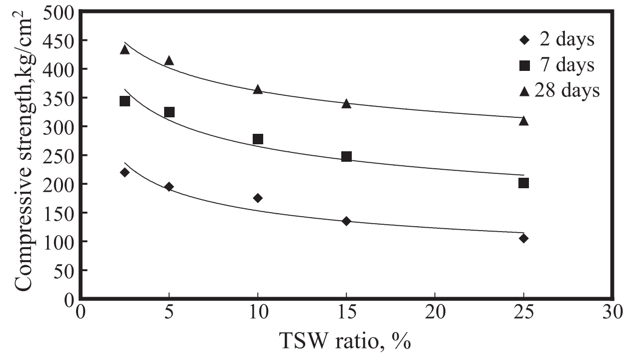

Fig. 4. Compressive strength of concrete with TSW.

ments and analysis during the experiments [14–17]. All of these experiments were carried out in Erçimsan-Aşkale Cement Factory in Erzurum, Turkey under real industrial conditions.

In addition, radioactive permeability of TSW and normal Portland cement were measured. The schematic arrangement of the experimental set up used in the work is shown in Fig. 2. The 59.5 keV γ-rays of an Am-241 radioactive source of about 3.7×10^9 Bq (100 mCi) were used to excite the secondary targets. The intensities of fluorescent X-rays were measured using a high-resolution Si(Li) detector (FWHM of 160 eV at 5.96 keV) and the data were collected into 1024 channels of a multichannel analyser. The spectra were collected for a period of 3600 s. Powder targets have been passed through a 400-mesh screen. The thicknesses of these powders are 0.09903 g/cm^2. The powder samples were mixed for 15 min and were compressed into pellets for 10 s at 20 tons by using a manual hydraulic press. Targets had an area of 225π mm^2. The secondary target-source distance was set to 13 mm, which was determined by measuring Kα X-ray intensities at different distances Secondary target-absorber distance were set to 44 mm [18].

When X-ray beam passes through an absorber, it is attenuated. The degree of attenuation depends on scattering and various absorption processes. Without going into the details of these processes, Lambert's law states that equal paths in the same absorbing medium attenuate equal

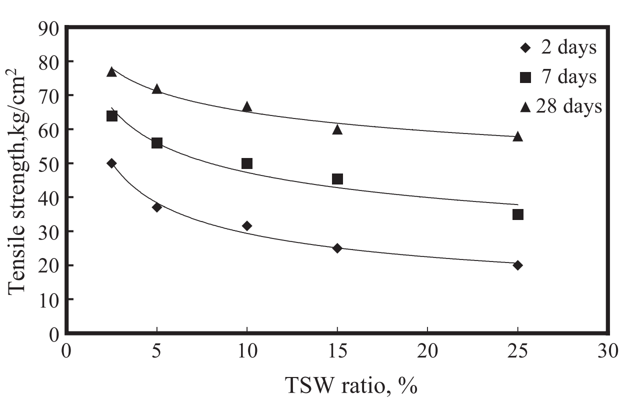

Fig. 3. Tensile strength of concrete with TSW.

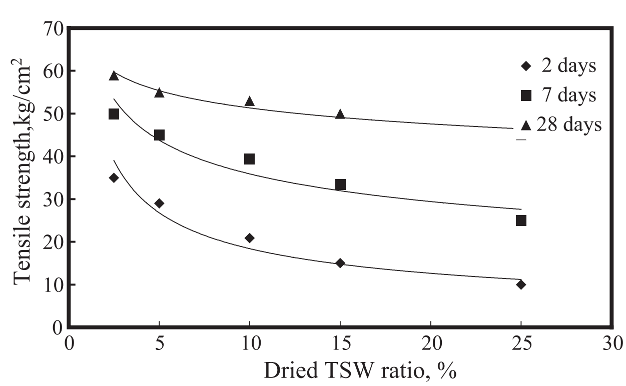

Fig. 5. Tensile strength of concrete with TSW dried at 105 °C.

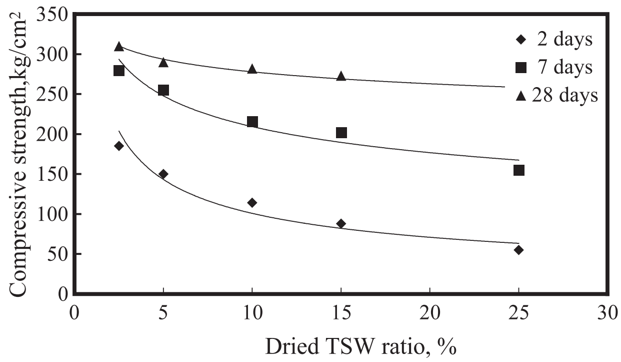

Fig. 6. Compressive strength of concrete with TSW dried at 105 °C.

fractions of the radiation. Suppose that the intensity I is reduced by an amount dI for the path length dx. Then, dI/$I \propto$ dx, or

$$dI/I = -\mu dx \quad (1)$$

After integrating,

$$I = I_0 e^{-\mu x} \text{ or } \ln(I/I_0) = -\mu x \quad (2)$$

where μ is the linear attenuation coefficient. The negative sign indicates that I decreases as x increases. $I=I_0$ at $x=0$. All of the quantities except μ can be measured. Such measurements show that μ depends on the state (gas, liquid or solid) of the material. Therefore, it is useful to define the mass attenuation coefficient μ_m, which does not depend on the particular phase of the material [19]. At this time, Eq. (2) shows that the intensity of the transmitted photons decreases exponentially with the thickness of absorption material, or the $\ln(I/I_0)$ decreases linearly with x. Transmission fraction I/I_0 is determined by

$$I/I_0 = e^{-\mu_m \rho x} \quad (3)$$

where ρ is the density of the material [20].

In this experiment, the net counts without absorber (I_0) and with absorber (I) were obtained at the same time and

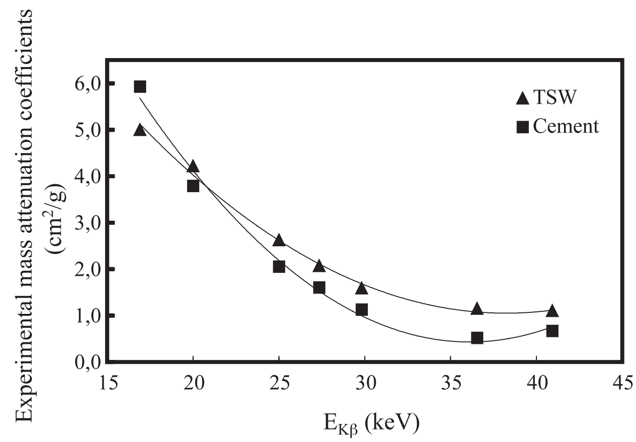

Fig. 8. Experimental mass attenuation coefficients of TSW and normal Portland cement.

experimental conditions. Theoretical values of mass attenuation coefficients for TSW and cement have been calculated using WinXcom [21].

3. Results and discussion

The cement samples were obtained by adding separately TSW to the clinker in ratios of 2.5%, 5%, 10%, 15%, 20%, 25%, 40% and 50% (w/w). The compressive strength and tensile strengths of the concretes produced by these cements were determined. Results obtained are given in Figs. 3–6. It is observed that the concrete from cement with TSW had a higher compressive strength and tensile strength than concrete produced with normal Portland cement. The compressive strengths of the concretes from pure clinker and Portland cement were 455 and 325 kg/cm^2, respectively, whereas compressive strengths achieved by addition of 2.5%, 5%, 10% and 15% (w/w) of TSW to the clinker were 434, 415, 365 and 340 kg/cm^2, respectively. Additionally, the tensile strength of the concretes from pure clinker is 78 kg/cm^2, while being 77 kg/cm^2 for cement with 2.5% (w/w)

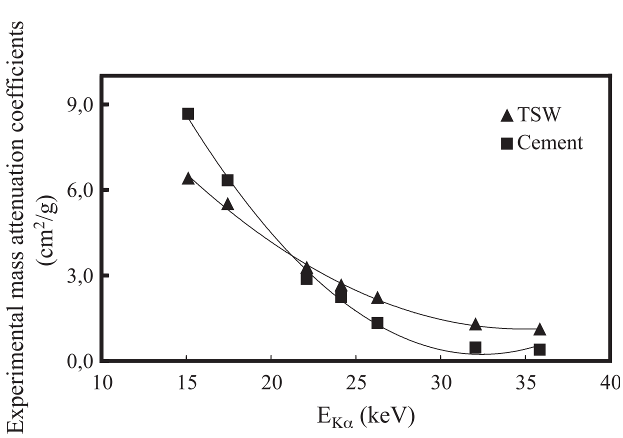

Fig. 7. Experimental mass attenuation coefficients of TSW and normal Portland cement.

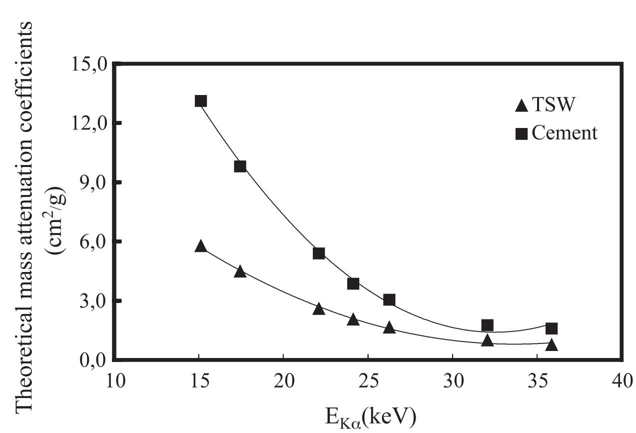

Fig. 9. Theoretical mass attenuation coefficients of TSW and normal Portland cement.

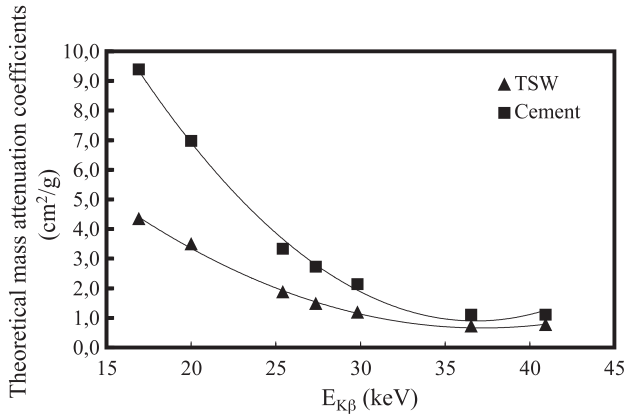

Fig. 10. Theoretical mass attenuation coefficients of TSW and normal Portland cement.

TSW. It was concluded that the TSW could be added to the clinker to produce modified cement.

The experimental and theoretical mass attenuation coefficients of TSW and normal Portland cement are also graphically presented for both Kα and Kβ energies in Figs. 7–10, and also, their experimental and theoretical transmission factors for both Kα and Kβ energies in Figs. 11–14. Mass attenuation coefficients of TSW and cement decrease with increase at energy of Kα and Kβ in the energy range 15.746–40.930 keV. On the other hand, transmission factors increase with increasing energy for the same energy region. This means that radioactive permeabilities of TSW and cement increase with increasing energy. A similar result for concrete has been obtained by Shiao and Tsai [5] who shows to decrease radioactive permeability of concrete by adding the boron compounds.

4. Conclusion

The concrete obtained from the cement with TSW gives the better mechanical strength than that of the others traditional cements, and mechanical strength of the concretes obtained decreases with increasing the TSW ratio. On

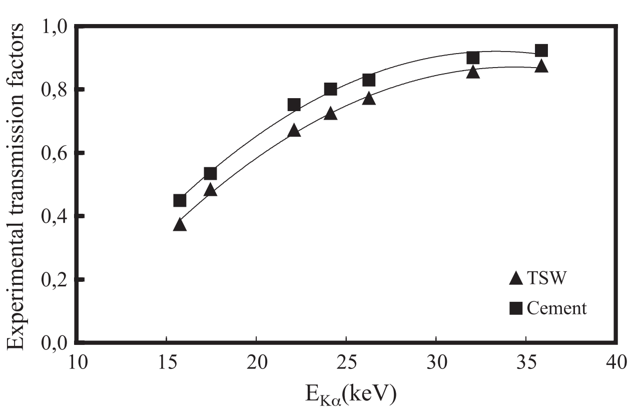

Fig. 11. Experimental transmission factors of TSW and normal Portland cement.

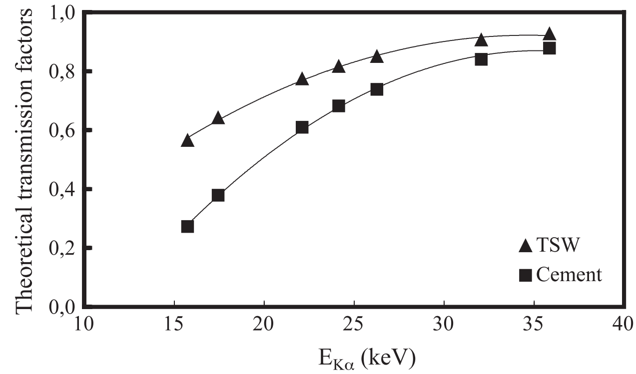

Fig. 12. Theoretical transmission factors of TSW and normal Portland cement.

the other hands, it is known that the obtained cements and concretes are resistive across microbial decomposition because contained boron compounds are antiseptics [2].

As shown in Figs. 7–10, the mass attenuation coefficients decrease with increasing the photon energy. Besides, the experimental mass attenuation coefficients of TSW are systematically higher than those from cement. This means that when the Kα and Kβ X-rays abound in the energy range 20<E<40.930 keV passing through TSW samples are absorbed more than those from cement. Also, that radio-

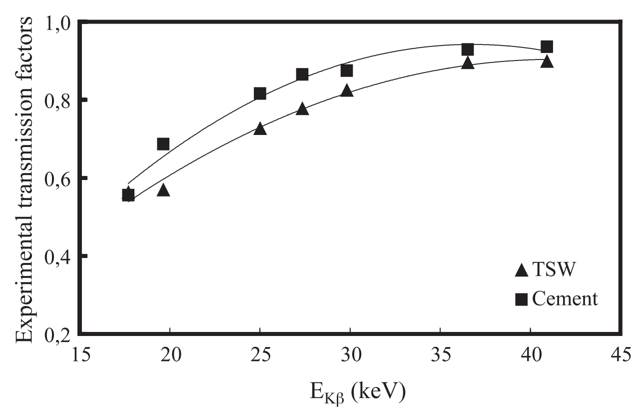

Fig. 13. Experimental transmission factors of TSW and normal Portland cement.

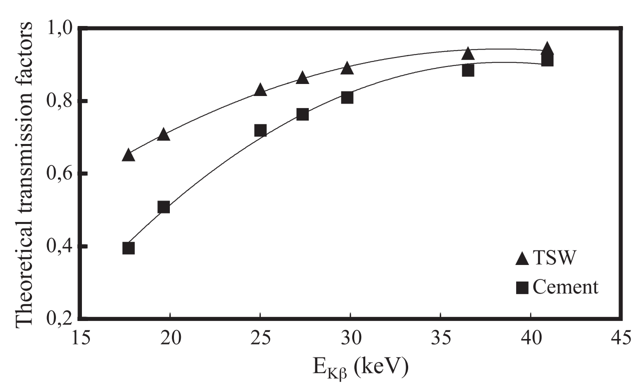

Fig. 14. Theoretical transmission factors of TSW and normal Portland cement.

active permeability of TSW is less than that of normal Portland cement implies that TSW-containing cement will have lower radioactive permeability in according to normal Portland cement and boron compounds decrease radioactive permeability of the concrete [5,12,13]. As a result, it is suggested that TSW can be added as an additive to cement up to 25% by weight.

Theoretical mass attenuation coefficient values of TSW are smaller than those from cement opposite to experimental values. This case was attributed the fact that the various cement components and phases and their formations could not be found completely. Furthermore, the different between experimental and theoretical values may be attributed to the effects of chemical environment on the mass attenuation coefficient values. The mass attenuation values are believed to be affected by the chemical, molecular and thermal environments. Those phenomena lead to the deviation of the experimental mass attenuation coefficients from the theoretical values calculated by considering the cross section for an isolated atom. This deviation is termed as the breakdown or no validity of the mixture rule. Such effects have been observed by earlier investigation [22].

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