Layered Thin Film Radiation Shields

Phase I Final Report

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Abstract

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There is an ever increasing use of modern imaging technologies which use ionizing radiation that have revolutionized diagnostic radiology. The benefits to patients however, come at a cost of chronic and cumulative exposure to clinicians. In fact, radiation exposure and spine complications, accompanied with back pain, are considered to be occupational hazards for interventionalists. Government agencies like the NIH, FDA and NCI have raised alarms about radiation exposure rising to epidemic levels. We have demonstrated the feasibility of effective 0.5 mm lead-equivalent radiation protection, at ~ 50% of the weight of lead-based materials, with our novel bi-layered thin film attenuating materials. These bi-layers were made using non-toxic and heavy metal-free $BaSO_4$ and Bi_2O_3 compounds. We have also developed theoretical framework that predicts that the bi-layered material may be more effective at attenuating the lower energy, more biologically harmful radiation than previously possible.

Significant Findings:

Our preliminary studies had showed that our innovative concept of mixed barium and bismuth salt formulations exhibited Xray dose attenuation equivalent to traditional lead-based radiation protection garments. In Phase I, we built on this base and extended the work to developing layered thin-film lightweight shielding materials, and established the technical merit and feasibility of demonstrating its radiation attenuation capability to be substantially equivalent to 0.5mm lead, but with a significant weight advantage compared to lead-based shielding materials.

We designed and fabricated bi-layer shielding materials by tailoring the compositions and weight fractions of the ceramic particulate $BaSO_4$ and Bi_2O_3 radiation absorber materials.

By using calibrated dosimeters, ion chambers and controls, we tested the radiation attenuation characteristics using well-established and well-accepted ASTM test protocols. And finally,

We compared and contrasted the attenuation characteristics with lead-based radiation shielding material and demonstrated % attenuation equivalent to 0.5mm lead at approximately half the weight.

Translation of Findings:

Traditional lead-based and “light-lead” radiation protection garments are known to lead to significant back pain for users. In fact, a survey of over a thousand interventionalists who routinely used fluoroscopy to treat their patients found that about half had doctor diagnosed back pain, with about 33% of them filing workmen’s compensation injury claims for rehabilitation. Thus, back pain stemming from the use of traditional radiation protection equipment is widely considered to be an occupational hazard for interventional clinicians.

The new bi-layered thin film attenuating shields developed in this study are a new, effective and light-weight radiation protection solution that can substantially alleviate such occupational injury and improve workplace safety.

The bi-layered thin film shields may also be used in other radiation environments beyond healthcare, such as in the nuclear energy and nuclear medicine industries.

Outcomes/Impact:

Use of bi-layered thin films could have significant positive impacts in reducing occupational hazards amongst radiation workers: by reducing the weight significantly without compromising shielding efficacy, the debilitating effect of back pain to users is minimized and ideally, avoided. Furthermore, by virtue of the fact that the bi-layer films actually eliminate the lower energy part of the radiation transmitted through the shield more effectively than other light-lead shields, the harm to human health from excessive radiation is further reduced.

Scientific Report

Introduction

Use of ionizing radiation technologies such as C-arm fluoroscopy and computed tomography (CTs) have rapidly become commonplace in operating rooms, outpatient clinics, and emergency departments. Clinicians especially are exposed routinely for several hours a day in their normal course of practice and hence they routinely use lead aprons and thyroid collars. Clinicians are, however, dissatisfied with the weight of these lead garments.[i] Concerns also exist regarding environmentally safe methods of disposal of lead-based shielding garments. Hence, there is a drive to investigate alternate lead-free shielding materials that are lighter and thus more comfortable for the user, and non-toxic, alleviating disposal concerns. We have initiated the development of lighter weight shielding materials made from barium and bismuth compounds that in preliminary tests have shown the potential for effective photon shielding. Consistent with theoretical considerations, we are able to layer these photon absorbing materials to provide more effective photon shielding with our unique processing technology. Furthermore, the materials set is non-toxic. This provides a unique opportunity to develop non-lead-based lightweight shielding materials with more effective photon absorption than previously possible.

In preliminary studies we showed that our innovative concept of mixed barium and bismuth formulations has radiation attenuation characteristics equivalent to elastomer-based heavy metal radiation protection garments. The Phase I project built on this base and extended the work to developing layered thin-film lightweight shielding materials, and established the technical merit and feasibility of demonstrating its radiation attenuation capability to be substantially equivalent to 0.5mm lead, but with a significant weight advantage compared to lead-based shielding materials.

The specific objectives were to:

1. Design and make bi-layer shielding materials by tailoring the composition and amount of the ceramic particulate absorber materials.
2. Using calibrated dosimeters, ion chambers and controls, test the radiation attenuation characteristics using well-established and well-accepted ASTM test protocols. And,
3. Compare and contrast the attenuation with lead-based radiation shielding materials.

This report shows that the radiation attenuation level achieved by the bismuth/barium bilayer is statistically equivalent to that obtained using currently available 0.5mm lead equivalent radiation shielding materials. We computed a weight specific attenuation parameter to yield the attenuation % per gram and scored all the materials tested. The bi-layered bismuth/barium material developed under this Phase I exhibited the highest specific attenuation. Thus, our novel concept represents a significant step forward in providing effective radiation protection to clinicians, at a significantly reduced weight.

Materials and Methods

Bi-layer thin films were constructed using barium sulfate powder and bismuth oxide powders compounded with a binder/plasticizer. Analytical and technical grades of barium sulfate and bismuth oxide were procured (Alfa Aesar, Ward Hill, MA and NOAH Technologies, San Antonio, TX,) and characterized for particle size, morphology and phase purity using analytical microscopy and X-ray diffractometry. Four different binder systems were investigated: neoprene, urethane, silicone, and vinyl based systems. The ceramic powders were carefully blended into the binder systems to achieve solids loadings of at least 70 weight % without agglomeration, producing a castable slip that was rolled onto a release substrate and cured to form a pliable sheet of controlled uniform thickness. Pliability and crack-resistance was evaluated using a Tabor V-5 stiffness tester (Tabor Industries, North Tonawanda, NY). Laboratory-scale attenuating sheets of up to 20 x 20cm size were formed by rolling the slip between two sheets of plastic-coated or silicone-coated release substrate. Sheet thickness was controlled by using shims. The rolled sheets were cured at ~ 130°C. Larger sheets (up to 0.5 x 1m) were made using a slip roller (Model 382-D, Pexto Inc., Southington, CT); sheet thickness was controlled both by shims and by adjusting the roller pinch. Multiple specimens (3.8 x 3.8cm) were cut from each sheet and used for X-ray attenuation studies. The solids loading and thickness of the attenuating sheet was iteratively optimized to provide the highest attenuation per unit weight of attenuating material. For screening tests using a clinical C-arm, two attenuating films were made. One comprised 75 wt% Bi_2O_3 of 0.76 and 0.96mm thickness, deposited directly onto a Tyvek[R] (DuPont) substrate. A second film of 0.96mm thickness, comprising 75 wt% of a 50:50 homogeneous mixture of Bi metal powder (Alfa Aesar, 99.5%) and Bi_2O_3 powders, was also deposited directly onto Tyvek[R].

From these films, 2.5cm x 2.5cm specimens were cut out for attenuation measurements. Test coupons were made from these specimens with a bi-layered composite construction comprising the 0.96mm Bi_2O_3 film and the 0.96mm 50:50 Bi-Bi_2O_3 film. Based on McCaffrey et al., this test coupon was used with the lower-atomic number Bi_2O_3 film on the upstream side and higher-atomic number (50:50 Bi–Bi_2O_3 film) on the downstream side.

Attenuation properties of this composite were measured between 60 to 130 kVp for 60 s exposures. Commercially available lead and lead-free shields from thyroid collars labeled as 0.5mm lead equivalent were used as controls. The ratio of transmitted radiation dose to incident dose provided the attenuation %. Means and standard deviations of attenuation performance, and pass through radiation for the test specimens and controls, were computed and compared using a two-tailed Student's t-test. Two types of measurements were made: [1] screening tests using a clinical C-arm fluoroscope (Phillips, at the University of Illinois Medical School, Orthopedics Dept.) and screened dosimeters with a limit of detection of 5 mrad (NanoDot, Landauer Inc., Glenwood, IL), and [2] An X-ray cabinet (Faxitron RX650, Tucson, AZ) with a 0.6cc ion-chamber (Model 10X5-0.6CT, RadCal, Monrovia, CA) with a limit of detection of 0.01 mrad. The ion chamber was coupled to a digital monitor/controller (Model 9010, RadCal, Monrovia, CA).

For the screening tests, the specimens were placed on a hand table with the source of radiation simulating an operative field configuration. The dosimeters, placed directly beneath the test specimens and the control, measured the transmitted radiation in mrad. Care was taken to place the swatches reproducibly in the field using a location template. Independent measurements of direct radiation exposure were made to ascertain the spatial uniformity of the field. Scatter radiation, if present, was detected by placing dosimeters around the perimeter of the X-ray field. Exposures were for 60 seconds at 60, 90 and 110 kVp, which are voltages commonly used for diagnostic and intra-operative imaging. Radiation doses were averaged over five independent replicate exposures, in accordance with ASTM Standard 2457-06, to ensure reproducibility. The dosimeters were sent to Landauer for dose readings. Means and standard deviations for the data were computed.

For the attenuation measurements using the Faxitron X-ray cabinet, considerable effort was taken to maximize reproducibility by ensuring identical positioning of the ion chamber and attenuating specimens with respect to the source. This was achieved by employing an acrylic housing lined at the base with 0.5mm lead, and to position the ion chamber in a reproducible orientation under a 3.8 x 3.8cm attenuating specimen (Fig. 1).

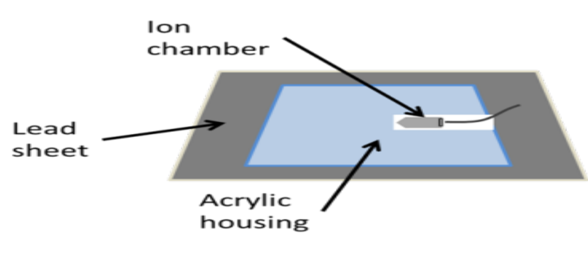

Fig. 1 Setup for repeatable attenuation studies

The bilayer specimen data collected from the screening tests conducted using the C-arm were compared to those from lead shield, Bi_2O_3, and Bi / Bi_2O_3 specimens. Data were collected using the Faxitron RX650 on the $BaSO_4$ / Bi_2O_3 bilayer, ten commercially available attenuating materials, and 0.5mm lead foil. Comparison of means was made using ANOVA.

Results and Discussion

In general, we found that barium sulfate powders exhibited equiaxed grain morphology with sizes ranging from 0.5 – 2 microns. In contrast, bismuth oxide powders exhibited either an equiaxed or acicular morphology, with particle size ranging from 3 – 25 microns (acicular, NOAH) and from 1.5 – 3.5 (equiaxed, Alfa Aesar). Powders with acicular morphology and sub-micron sized mean particle sizes were found to limit the solids loading to below 70 wt% or result in attenuating films with a gritty texture that could result in irritation against skin, and thus unsuitable for incorporating into attenuating garments. Iterative trials led to the choice of barium sulfate with a mean particle size of 4 – 6 microns, and bismuth oxide with a mean particle size of 5.5 microns, resulting in attenuating sheets with a solids loading of at least 70%. Neoprene and urethane binder systems provided stiffer sheets at 70 wt% $BaSO_4$ or Bi_2O_3. In contrast, both silicone and vinyl binder systems could be loaded with over 80 wt% $BaSO_4$ or Bi_2O_3, and yielded flexible sheets with fabric-like drape. Sheet thickness was controlled by adjusting spacer shim thickness during rolling. For subsequent tests, attenuating sheets with the vinyl binder system were selected.

No significant scatter or spatial variation in the readings was exhibited by the four dosimeters placed around the perimeter of the radiation field of the C-arm. Three dosimeters placed within the field also did not indicate any outliers, confirming spatial uniformity. Measured dose attenuation values normalized to the unshielded dose were 67%, 76%, 80%, 88% and 89% for the 0.76mm Bi_2O_3 film, 0.96mm Bi_2O_3 film, 0.96mm Bi:Bi_2O_3 film, lead shield and two-layered Bi_2O_3 + Bi-Bi_2O_3 film, respectively, as shown in Table 1. While the absolute values of attenuation for Lead Shield and the Two Layers of Bi Bi_2O_3 and Bi_2O_3 may not indicate a large difference, these differences were found to be statistically significant ($p<.01$).

Table 1
Attenuation of Four Material Combinations vs. Lead Shield
Voltage: 110 KVp

Specimen	Attenuation
0.76mm Bi_2O_3	67%
0.96mm Bi_2O_3	76%
0.96mm Bi Bi_2O_3	80%
Lead Shield	88%
Two layers of Bi Bi_2O_3 and Bi_2O_3	89%

Thin film attenuation sheets with 75 - 85 wt% $BaSO_4$, and 75 - 87 wt% Bi_2O_3, were prepared at various thicknesses and X-ray attenuation was measured. 85 wt% $BaSO_4$ and 87 wt% Bi_2O_3 solids loadings were found to be upper limits for making flexible sheets: higher loadings resulted in sheets that were not adequately pliable. Significantly higher sheet thicknesses (incurring an undesirable weight penalty) were required at lower than 70 wt% solids loading for high X-ray attenuation. Fig. 2 illustrates the effect of solids loading on X-ray attenuation at 100 kVp in a direct beam.

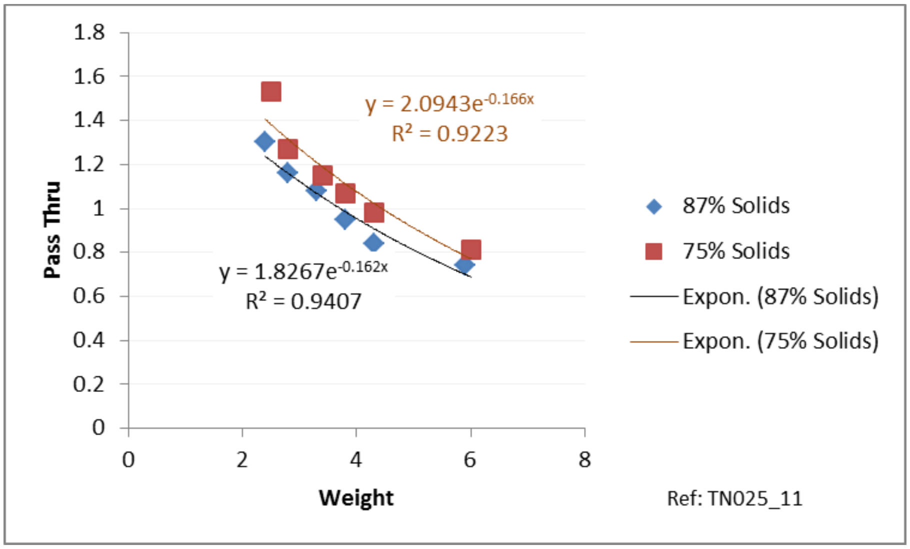

Fig. 2: Effect of solids loading and film weight of Bi_2O_3 on attenuation in a 100 kVp direct X-ray beam.

Subsequent efforts focused on using the $BaSO_4$ and Bi_2O_3 materials as a couple with particular focus on optimizing cost and weight combinations for best attenuation. Fig. 3 shows the attenuation performance and costs of 87 wt% Bi_2O_3 films coupled with 80 wt % $BaSO_4$ films in a 100 kVp direct beam. The optimal combination of weight, low pass through and low cost occur around a total coupon weight of 6 grams – which corresponds with 3.6g weight for Bi_2O_3 positioned downstream of the $BaSO_4$ film.

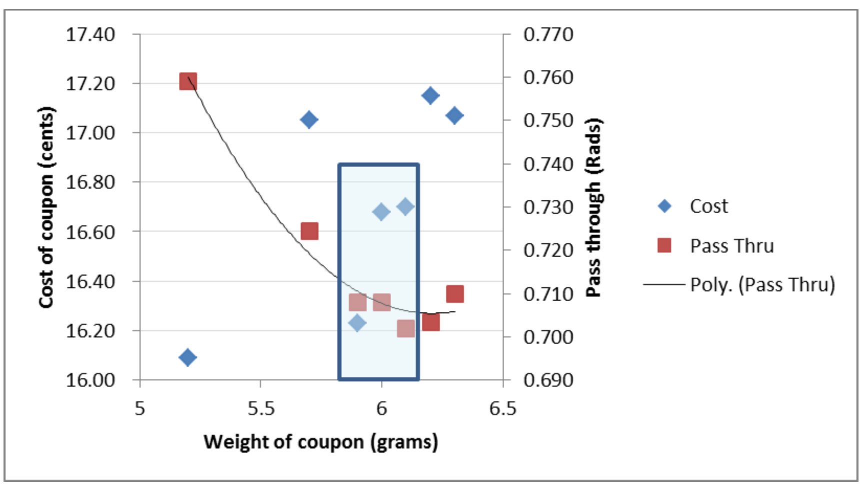

Fig. 3. Attenuation of 100 kVp direct X-ray beam by 87 wt% Bi_2O_3 films..

Attenuation performance (under direct beam) of all eleven materials, and the 6g $BaSO_4/Bi_2O_3$ bilayer, was characterized using the Faxitron X-ray cabinet at 60 kVp and 100 kVp settings with exposure durations of 60 seconds. The results are summarized in Table 2, and show that the bilayer material provides attenuation comparable to both commercial attenuating materials and 0.5mm lead sheet.

Table 2
Comparative Attenuation Performance of $BaSO_4/Bi_2O_3$

Specimen	@ 60 KVp	@ 100 KVp	Aggregate
BloXR	90.3%	83.4%	86.8%
Starlite	89.4%	83.7%	86.5%
Cost Crun	91.4%	87.6%	89.5%
Pulse blu	90.9%	86.2%	88.5%
Pulse blk	91.0%	86.8%	88.9%
Greenlite	90.9%	84.3%	87.6%
Demron	91.4%	87.2%	89.3%
Wolf	91.0%	86.3%	88.6%
Xenolite	91.1%	86.5%	88.8%
Prestige	89.0%	83.8%	86.4%
Envirolite	90.4%	86.0%	88.2%
0.5mm Pb	91.6%	86.8%	89.2%

Importantly, when the measured attenuation by each sample is normalized to the weight of the 3.8x3.8cm specimen size to yield attenuation/gram, (or specific attenuation), the combination of 2.4g 80 wt% $BaSO_4$ upstream of 3.6g 87 wt% Bi_2O_3 provides the highest specific attenuation (Fig. 5). In this chart, the green column is the bi-layer thin film specimen, the blue columns are lead-free specimens, the black column is 0.5mm elemental lead, and the gray columns are lead-based attenuation materials. The weight advantage over commercial lead-based attenuation material is about 50%. This exceptional attenuation/weight relationship holds true both at 60 and 100 kVp. The only commercial attenuating material providing similar specific attenuation is Greenlite (manufactured by Infab Corp, Camarillo, CA). However, elemental analyses conducted independently at the Dept. of Physics, University of Utah, indicated that the Greenlite-based thyroid collar contained toxic metals - lead and antimony - in contrast to the non-toxic $BaSO_4/Bi_2O_3$ BloXR attenuating material.

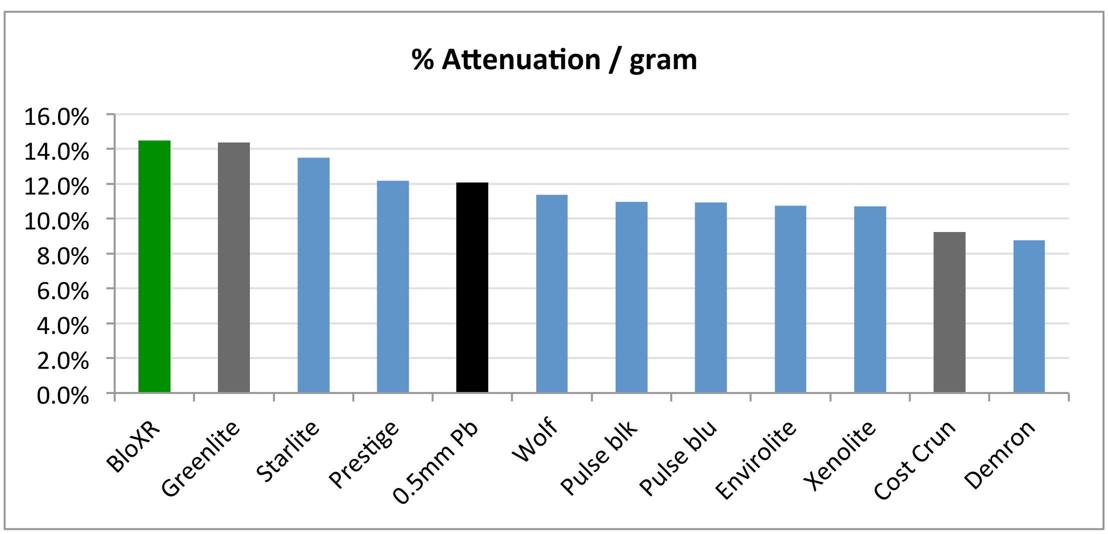

Fig. 5. The weight of a 3.8x3.8cm coupon of 10 commercial attenuating materials, 0.5mm Lead, and the $BaSO_4/Bi_2O_3$ bi-layer attenuating material, plotted against the percent X-ray attenuation of each material averaged at 60 kVp and 100 kVp.

Since a total of twelve test specimens were being compared for attenuation performance, ANOVA (rather than a t test) was conducted on the aggregated attenuation data at 60 and 100 kVp direct beam, and the results are presented in Table 3. The F value was found to be 0.941 compared to F_{crit} of 1.952; since the F value was less than F critical, a post hoc HSD test was not necessary. Results from the ANOVA indicate no statistically significant difference between the $BaSO_4/Bi_2O_3$ bilayer and all other materials tested, as shown in Table 3.

Table 3

ANOVA Results

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.008	11	0.001	0.941	0.509	1.952
Within Groups	0.047	60	0.001			

Traditionally lead-based materials are made by incorporating powdered lead (Pb) in a flexible elastomer matrix. More recently, in an effort to reduce weight, lead-free garments comprising of heavy metals such as tin, tungsten or antimony have been substituted for lead. These lead-free materials while generally meeting the 0.5mm lead-equivalent standard, are less effective immediately below the K-absorption edge of the material. McCaffrey et al have shown that low and hi atomic number metal based bi-layers provide a more consistent improvement over lead across the whole spectrum through the judicious application of the characteristics of the photoelectric effect[ii]. Figure 6 shows the Monte-Carlo calculated spectra from a single layer (Bi metal, Z=83, which is similar to Pb, Z=82) and bi-layers of Ba + Bi metals. The Ba layer provides effective attenuation in the 40 - 100 kV range, but introduces enhanced photon peaks near the K- absorption edge at approximately 36 kV. The Bi layer provides effective attenuation below 40kV.

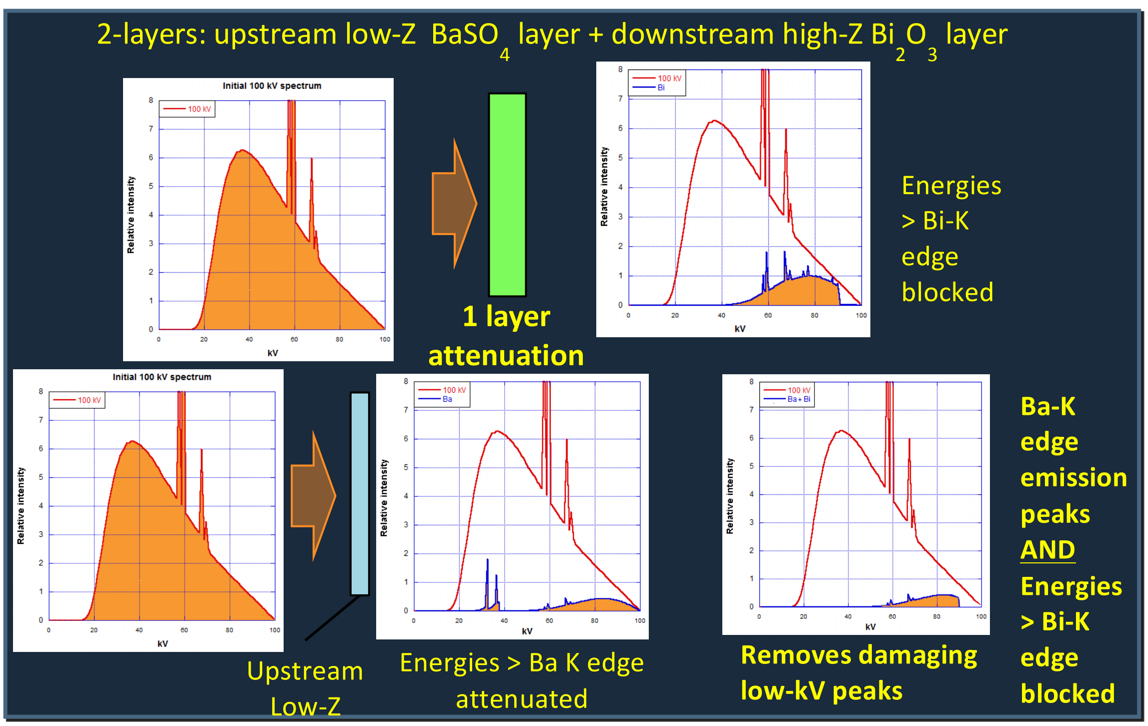

Fig 6: Monte-Carlo Calculated Spectra for 1 layer (top) and bi-layer (bottom) attenuation materials. The bi-layer approach provides ~15% lower radiation dose to the user.

By creating a bi-layer with half the radiological thickness composed of Ba (upstream, closest to the X-ray tube) and the other half the thickness composed of Bi (downstream), the complimentary effects of the two materials results in improved total attenuation. This is manifested as reduced total area under the curve of ~ 15% (Fig 6).

Mccaffrey et al predicted these results for elemental metals. Our work, surprisingly, showed that the effects also works for Ba and Bi compounds, particularly when combined with polymers that allow higher loadings than possible with conventional elastomeric sheeting materials, while still maintaining sheet flexibility and pliability.

Summary and Conclusions

- Screening experiments with a C-arm indicated that bismuth-based thin film attenuating materials were promising candidates
- A solids loading of 80 weight % for $BaSO_4$ and 87 weight % for Bi_2O_3 was found to be the maximum achievable for producing pliable sheets
- The combination of $BaSO_4$ and Bi_2O_3 in the upstream / downstream orientation provides attenuation levels comparable to commercially available 0.5mm equivalent materials.
- The specific attenuation (% attenuation per gram of material) provided by this combination is the highest amongst the 10 commercially available materials tested.
- The weight advantage of the bi-layer shielding over commercial lead-based materials is about 50%.

Thus, in Phase I we have successfully demonstrated the feasibility of providing effective radiation protection to clinicians, at a significantly reduced weight, using our novel concept of layered thin film attenuating materials, made using non-toxic and heavy metal-free environmentally friendly materials. Further development and testing in Phase II, focusing on cost effective large scale manufacturing of these materials, making actual garments, and demonstrating efficacy in clinical settings will enable translating the novel materials set and concept to commercial introduction.

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