Development of luminescent diamond simulants for X-ray recovery

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Synopsis

Specially designed X-ray machines are used extensively on diamond mines for the recovery of diamonds from ores. These machines are extremely expensive and, at present, there are no reliable methods of determining if the equipment is performing efficiently. The objective of this work was to manufacture translucent X-ray diamond simulants, which would emit varying but known luminescence signals when exposed to X-rays. These X-ray diamond simulants could then be used to determine the efficiency of diamond recovery operations.

Introduction

The recovery of diamonds from an ore can be compared to finding a needle in a haystack. A viable kimberlite deposit can have a grade as low as 10 carats per hundred tons (cpht), which equates to 2 parts per 100 000 000. A viable alluvial deposit could have grades as low as 1 cpht since only minimal crushing is required, and this equates to 2 parts per 1000 000 000.

A diamond mine

The flow sheet of a diamond mine includes extracting the ore from either an alluvial or a kimberlite deposit. In a kimberlite deposit, the ore is crushed using primary (jaw or gyratory) crushers. This crushed material is scrubbed to remove the clays associated with kimberlites and a large percentage of the non viable fine (-1.5 mm) material. The material is passed through secondary (cone) crushers with a 'top size' setting of 32 mm or 25 mm, depending on the expected top size of diamond, the mine expects to recover. The material is then screened, sized, and passed through a dense medium separation (DMS) circuit to remove all material with a density less than 3.0 g/ml. The majority of alluvial and kimberlitic material has a density less than 3.0 g/ml and the DMS circuit removes between 98% and 99% of this material to tailings. The DMS concentrate is then passed onto the recovery section where, due to the increased grade of the ore, security is increased.

If there is a magnetic component in the ore, this will report to the DMS concentrate since magnetic materials usually have a density greater than 3.0 g/ml. Magnetic separation can be used to further concentrate the ore by removing another 40% of the DMS concentrate to the magnetic fraction. The diamonds, which are heavy and non-magnetic, are contained in the non-magnetic fraction. This fraction is then sent to either an X-ray machine or a grease recovery plant or both. The +8 mm material coming out of the recovery plant is then sent to recrush (tertiary crushing) to ensure that no diamonds are locked up in large particles. This material then joins the crushed ore for reprocessing through the DMS and recovery plant. A block diagram showing the progress of ore through a diamond plant is given in Figure 1. The mass retention of the ore at each stage is given by the percentages associated with each stream.

In the block diagram in Figure 1, the total concentrate comprises 0.0033% of the ore. This equates to concentrating the ore 30 300 times. If the ore had a grade of 10 cpht, the occurrence of diamonds in the concentrate would be about 1 in 1650, and this final product is hand-sorted in the sort house.

An X-ray recovery machine

In a well-equipped recovery plant, the most common form of diamond recovery equipment is an X ray machine, as seen in Figure 2. When diamonds are irradiated with X-rays, they luminesce at an optical wavelength of 450 nm. The X-ray machine utilizes this property of a diamond to discriminate it from other particles. Ore is fed into an X-ray machine via a feeder, which ensures that all the material presented to the discrimination area, does so in a mono-layer. Here the material is irradiated with X-rays, which cause

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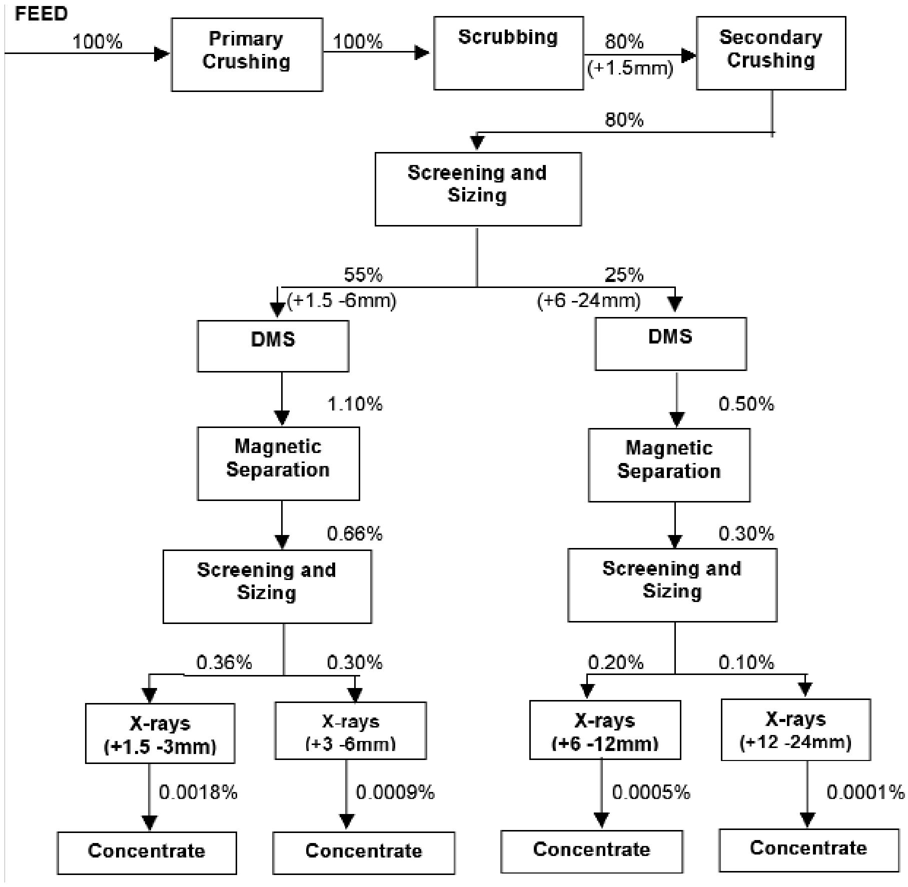

Figure 1—The flow of material in a diamond plant showing the percentage mass retention at each stage

the diamonds to luminesce. Any luminescence signal is filtered through an optical filter, the K45 filter, centred at 450 nm. The photomultiplier tube (PMT) then detects any light passing through the filter and sends a signal to the ejector to fire. The ejector (air or mechanical) removes the luminescent particle from the main stream into a concentrate area for final hand-sorting.

Tracers or simulants

Tracers or simulants are invaluable commodities when setting up mining equipment since they imitate the behaviour of the valuable mineral in the orebody. Tracers are added to the ore in far higher concentrations than the mineral, so providing the mine with greater confidence that the equipment is functioning correctly while also providing statistical information on the mine's recovery efficiency. The most common tracers in use on the mines are the density tracers, which are used to set up density separation equipment such as DMS cyclones, cones and pans. The density tracers are used to evaluate and compare the performance of different density separation equipment as well as the performance of equipment with various operating parameters[1].

Tracers have recently been developed for magnetic separation equipment[2] and can be used on wet or dry magnetic separators with either low or high intensity magnetic fields. Magnetic tracers have proved to be beneficial as they enable one to compare the performance of different

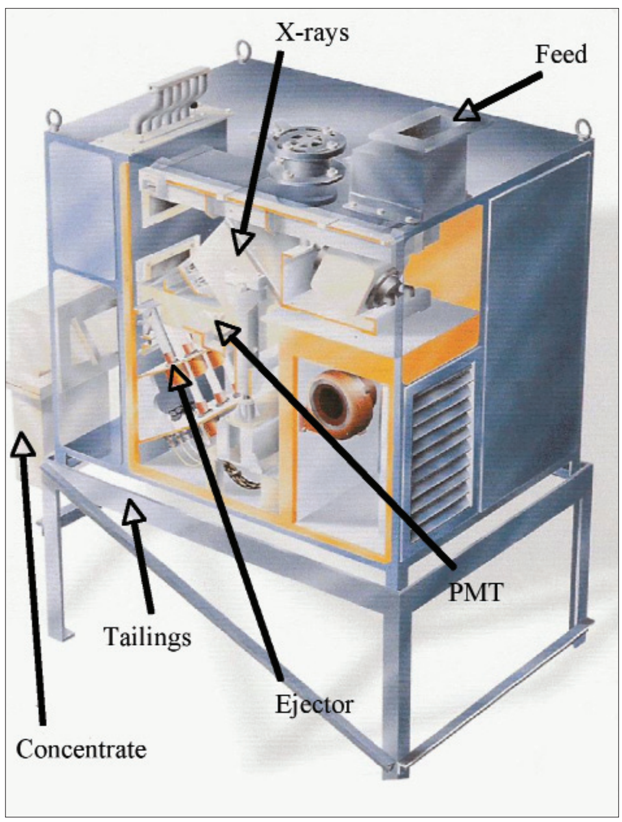

Figure 2—An X-ray machine with side panels cut away

magnetic separation equipment and to quantify the effects of changing operating parameters such as throughput or splitter plate position. Such tracers have also facilitated research into improving the design of the magnetic separating equipment.

In the past three years, hydrophobic tracers have been developed for auditing the performance of grease recovery equipment[3]. These tracers enable one to ensure that the grease characteristics are correct and that the water flow rates are correct for the efficient recovery of diamonds in a specific size fraction.

Surprisingly at present, there is no satisfactory method of setting up and commissioning an X-ray machine at a mine. There is also no satisfactory method of comparing the performance of different X-ray machines to ensure that the correct X-ray machine has been selected for a particular mine. An X-ray machine can cost between R1 million and R3 million and once this expensive item of mining equipment has been set up on a mine, there are no satisfactory guarantees that the machine is in fact recovering diamonds from the ore.

Once an X-ray machine has been commissioned, one then needs to monitor its performance over time in order to assess when to replace critical components such as the X-ray tubes, optical lenses or the photo multiplier tube. At present, De Beers manufacture opaque X-ray tracers, called 'LI Tracers' (luminescence intensity tracers). These tracers produce a range of known luminescence intensities for assessing the recovery efficiency of an X-ray machine at various optical sensitivities. De Beers sell these LI Tracers only to their own mines.

A need in the market was therefore identified for X-ray transparent diamond simulants. It was therefore decided to develop an X-ray diamond simulant that could be used reliably with all X-ray machines as a standard for comparing and setting up all X-ray machines. These X-ray diamond simulants imitate the luminescence response of a diamond when irradiated with X-rays. The functions of the diamond simulants are to assist with:

- Selecting the correct X-ray machine for a mine
- Commissioning an X-ray machine
- Optimizing the performance of an X-ray machine for its location and
- Monitoring the performance of the X-ray machine over time.

This paper discusses research on the development of X-ray transparent diamond simulants.

The properties of the X-ray diamond simulants

The aim of this research was to develop X-ray diamond simulants that simulate the responses of a diamond when irradiated with X-rays. The X-ray diamond simulants therefore required the following characteristics:

- They should be transparent to X-rays
- Their density should be similar to that of diamond (3.53 g/ml) to ensure that their movement (velocity, trajectory, momentum) is similar to that of a diamond
- They should luminesce at a wavelength of 450 nm in a manner similar to that of diamond when irradiated with X-rays
- Their luminescence signal should be detectable from all directions—omni directional
- They should be 'colour code-able' so that each colour is associated with a discrete luminescence signal intensity
- They should have a range of sizes to simulate the various size fractions of material treated by an X-ray machine and
- They should have a regular but non-spherical shape since a spherical object would roll on a feeder (unlike the octahedral diamonds) and produce incorrect timing parameters between the PMT and the ejector.

Equipment

In order to conduct this research, specialized equipment that could measure both reflected and transmitted luminescence signals from a diamond or diamond simulant had to be designed and built. A photograph of the experimental equipment is seen in Figure 3.

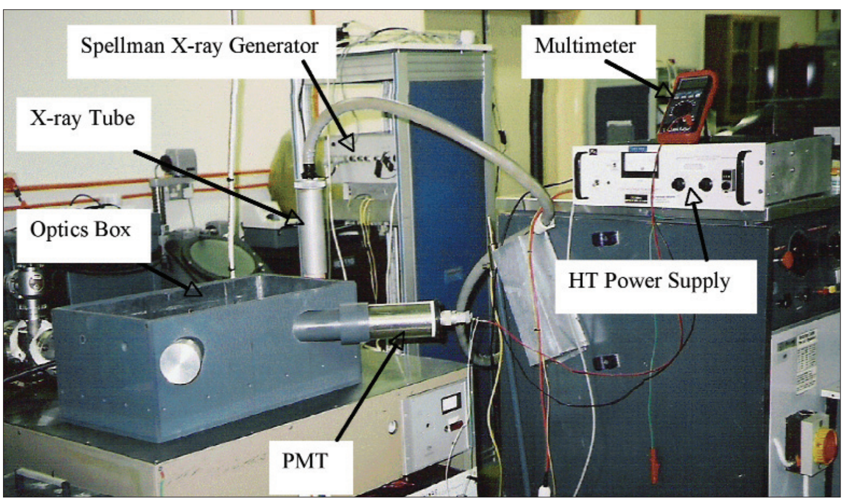

Figure 3—The X-ray equipment and test facility

The equipment consisted of a lead lined optics box where samples could be irradiated with X-rays. Inside the optics box was an adjustable stand on which the diamonds or luminescent diamond tracers were placed. Depending on the size of the diamond or tracer, the stand was either adjusted upwards or downwards to ensure that the centre point was in line with both the X-ray tube window and the PMT. The PMT could be positioned at either 45° (position 1) or 135° (position 2) to the X-ray tube (Figure 3). Position 1 was used for measuring reflected luminescence responses whereas position 2 was used for measuring transmitted luminescence responses.

The X-ray tube was a water-cooled unit connected to a digital Spellman X-ray generator, which enabled one to operate the X-ray tube with predefined current and voltage settings of 24 mA and 45 kV respectively[4]. The PMT required a high tension (HT) power supply which was set at 900 V for these measurements. The output from the PMT was a very small current whose magnitude corresponded to the intensity of the signal. The PMT output was measured with a multimeter, which had a 20 mega-ohm impedance. The readings on the multimeter were in volts and it was these voltages that were used to evaluate the luminescence from the different diamond simulants.

The PMT could detect visible light from 350 nm to 750 nm in wavelength. However, interest was centred around the luminescence response at 450 nm. A standard optical filter centred at 450 nm, the K45 filter, was incorporated in the equipment setup[5]. This filter was fitted to the PMT in a similar manner as in most X ray machines. The main purpose of the K45 filter was to improve discrimination between diamonds and gangue[6,7]. Due to the hazards of X-rays, the testing equipment was evaluated for radiation leakages using a Geiger counter[8].

For the manufacture of the X-ray diamond simulants, aluminium templates, silicone moulds, Teflon sheets, blenders, and an oven with a rotisserie were used. The aluminium templates were used to produce the 4 mm, 8 mm and 10 mm cube moulds (Figure 4) when required.

Materials

The materials used for the diamond simulants were tested for their suitability to provide the required response. Tests on different materials and different combinations of materials were conducted. The result of all the investigations culminated in an X-ray diamond simulant that was a composite consisting of:

- ➤ Calcium tungstate to provide luminescence
- ➤ Lead inserts to increase the density of the simulant
- ➤ Blue, green, white, red, yellow and black pigments to code the simulants of different luminescence intensities
- ➤ Polyurethane resin to bind the components together.

The ingredients were mixed in the required proportions and poured into the relevant moulds to form small cubes.

Calcium tungstate ($CaWO_4$)

Calcium tungstate ($CaWO_4$) was obtained in powder form and mixed into the resin. Calcium tungstate luminesces strongly when irradiated with X-rays with a peak luminescence signal at 420 nm, as seen in Figure 5[9]. The calcium tungstate powder was coarse and particles varied in size from 50 μm to 350 μm.

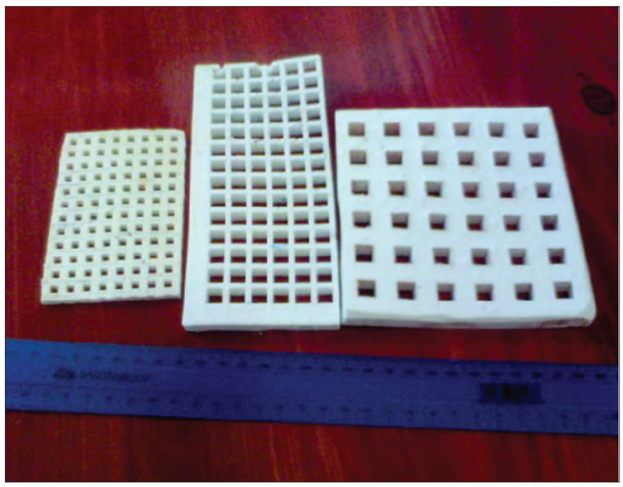

Figure 4—The 4 mm, 10 mm and 8 mm silicone moulds used for the manufacture of the X-ray diamond simulants

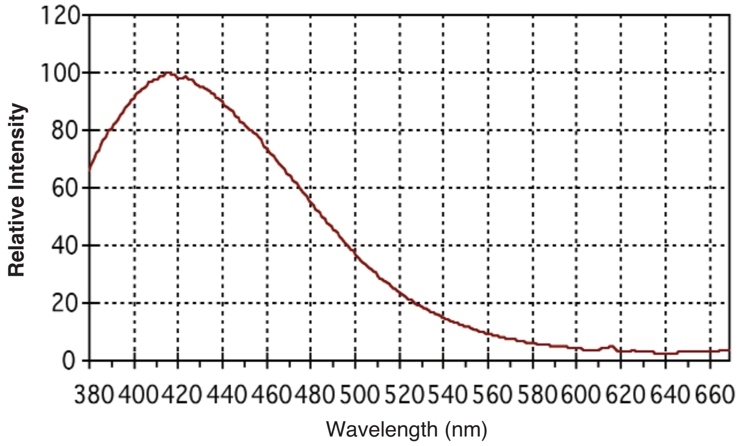

Figure 5—The fluorescence characteristics of calcium tungstate ($CaWO_4$)

This peak luminescent wavelength is slightly shorter than the required 450 nm (the peak luminescence signal of diamond). However, the curve shows that there is sufficient luminescence between the wavelengths of 450 nm and 500 nm to enable a calcium tungstate powder to be used in the X ray diamond simulant.

Lead inserts

The X-ray diamond simulant has to have a density of approximately 3.5 g/ml to correctly simulate the movement and trajectory of a diamond in an X-ray sorting machine. The density of polyurethane is 1.06 g/ml[10] and although the density of the calcium tungstate is 6.7 g/ml, only minute quantities of this ingredient were required. Therefore, a higher density material had to be included in the recipe to compensate for the low density of the polyurethane. Lead with a density of 11.35 g/ml[11], in the form of small cubes, was used in the interior of the simulants to yield the required density.

Pigments

A fundamental requirement of the pigments was that they be compatible with the other ingredients in the X-ray diamond simulants. The pigments were sourced from Advanced Material Technologies who manufacture an assortment of polymers and resins.

The pigments were very concentrated and thus their addition to the recipe was difficult to control from batch to batch of diamond simulants. Better control in pigment additions was obtained by diluting the different pigments in resin in the ratio of 1 g of pigment to 50 g of resin. This mix was then used to colour the simulants.

Polyurethane

The resin had to be transparent to X-rays and able to bind the other ingredients together.

Experimental procedures and results

Tests on the lead inserts

Tests were conducted to determine if the percentage of lead required would be small enough so as not to stop all the X-rays from passing through the X-ray diamond simulant. Batches of X-ray diamond simulants were made with each pigment, with 0.5 g of $CaWO_4$ for a pallet that could hold 100 simulants of size 8 mm cube. Lead inserts were placed in 5 of the simulants in each batch. The luminescence responses of simulants with and without lead inserts were then measured and compared. Table I documents the results obtained for the blue and green X-ray diamond simulants with the PMT in position 1.

Pigments

Batches of X-ray diamond simulants, without lead inserts and containing 0.5 g of $CaWO_4$ were evaluated for their luminescent signal strengths. In this test it was found that simulants of different colours responded differently when irradiated with X-rays. Some pigments increased the luminescence response whereas others attenuated it relative to the response of clear simulants with no pigment. The average luminescence for each batch of differently coloured simulants is documented in Table II.

These results showed that the luminescence response of a diamond simulant depended on both the amount of $CaWO_4$ and on the pigment. The pigments that produced a strong luminescent response were allocated to the simulants that had to emit a high luminescent signal while the pigments with a weak luminescent response were allocated to the simulants that had to emit a low luminescent response.

Table II

The luminescence responses of the simulants containing different pigments

Colour	Average	SD	%SD
Blue	33.06 V	4.87 V	14.74
Green	13.49 V	1.93 V	14.34
Clear (no pigment)	12.42 V	0.75 V	6.06
Red	9.38 V	0.76 V	8.06
Black	9.04 V	2.17 V	23.95
Yellow	8.06 V	1.13 V	14.05

SD = Standard deviation

Table I

Luminescence results of the X-ray diamond simulants with and without lead inserts

	Blue simulants (0.5 g $CaWO_4$)			Green simulants (0.5 g $CaWO_4$)		
Tracer	No-lead	Lead	Difference	No-lead	Lead	Difference
(V)	(V)	(V)	(V)	(V)	(V)	
1	28.31	19.45	8.86	12.35	9.70	2.65
2	28.65	23.27	5.38	12.80	10.90	1.90
3	32.20	28.69	3.51	16.90	13.40	3.50
4	37.05	28.16	8.84	13.10	10.60	2.50
5	39.08	38.95	0.13	12.30	9.60	2.70
Average	33.06	27.70	4.34	13.49	10.84	2.65
SD	4.87	7.34		1.93	1.54	
%SD	14.74%	26.49%		14.34%	14.18%	
% Signal loss due to the lead			13.13%			19.64%

SD = Standard deviation

Development of luminescent diamond simulants for X-ray recovery

When researching the requirements of the luminescent diamond simulants, two functions were identified. The function of the bright (blue) simulant was to assess how quickly the PMT recovers from a strong luminescence signal (from being blinded) and to ensure that no premature detection of the simulant/diamond occurs, which would result in incorrect timing between the PMT and the ejector. The function of the low luminescent simulants was to evaluate the noise level of the X-ray machine and the detection threshold of the X-ray machine. The required luminescent response from each colour coded simulant was based on these requirements.

The background luminescence response of the optics box was 5.0 V and was a result of the luminescence from the adjustable stand in the optics box and stray X-ray radiation reaching the PMT. Table III documents the luminescent responses required from each colour coded simulant when it is irradiated by X-rays in the optics box.

Polyurethane

The requirement of the resin was that it be transparent to X-rays and resistant to X-ray irradiation. A test was carried out to determine the attenuation coefficient of the polyurethane, which is given by the relationship:

$$I = I_o e^{-ux} \qquad [1]$$

Where: I = Transmitted X-ray intensity (lumens)
I_o = Incident X-ray intensity (lumens)
u = Attenuation coefficient (units)
x = Thickness (m)

The incident radiation I_o was determined by placing a photographic plate 20 mm from the X-ray tube and exposing it to X-rays for 500 ms. A similar plate was exposed for the same period with an 8 mm thick polyurethane disc placed between the X-ray tube and the plate to determine the value of I. After processing the two plates, their densities were compared on a light table and found to be similar. The attenuation coefficient for the polyurethane was thus assumed to be zero.

The deterioration of the polyurethane when exposed to X-rays was assessed by exposing samples to radiation for 15 minutes and 1 hour. During this period, significant browning of the polyurethane was observed, as seen in Figure 6.

Calcium tungstate quantities

The particle size range for the calcium tungstate was higher than expected. It was therefore difficult to obtain a homogeneous mix of powder and resin. Variations in the luminescence response from the simulants in the same batch could thus be expected as a result of the powder granulometery.

Once the ingredients were identified, the amount of calcium tungstate, required for each pigment, had to be determined. This was necessary in order for the simulants to produce different luminescence intensities when irradiated with X-rays. In this test, batches of X-ray diamond simulants were made up with different quantities of calcium tungstate for each pigment and graphs of the luminescence responses were drawn for each batch of simulants. The graphs were analysed and the amount of calcium tungstate for each diamond simulant was obtained from the graph, as seen in Figure 7 for the yellow simulants.

For the yellow diamond simulants an amount of 0.2 g of $CaWO_4$ was required to obtain a luminescence response of 6.92 V (see Table III) as denoted by the horizontal blue line in Figure 7.

The amount of calcium tungstate needed with each pigment was determined in a similar manner. The amount of calcium tungstate to be added to each pigment in order to obtain the required luminescence response is documented in Table IV.

Rule of mixtures

The rule of mixtures was used to determine the proportions of the various constituents in the recipe in order to obtain a density of 3.53 g/ml in the simulants. Using the rule of mixtures, Equation [2], and the fact that the amount of calcium tungstate had already been determined, the amounts of lead and polyurethane to be added to the recipe were calculated. Using Equation [2], batches of diamond simulants were made up for each colour, as seen in Figure 8.

$$\rho = A\rho_1 + B\rho_2 + C\rho_3 \qquad [2]$$

Where ρ = Density of diamond (3.53 g/ml)
ρ_1 = Density of calcium tungstate (6.7 g/ml)
ρ_2 = Density of lead (11.35 g/ml)
ρ_3 = Density of polyurethane (1.06 g/ml)
$A + B + C = 1$

A for each pigment was determined from Table IV.

Table III

The luminescent response required from each colour coded simulant

Colour	Required luminescence response
Blue	38.01 V
Clear	21.96 V
Green	9.93 V
Red	8.32 V
Black	7.52 V
Yellow	6.92 V
Background	5.00 V

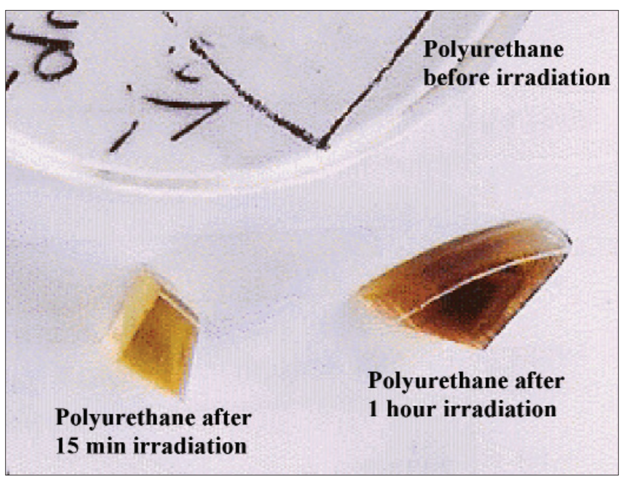

Figure 6—Samples of the polyurethane that were irradiated with X-rays

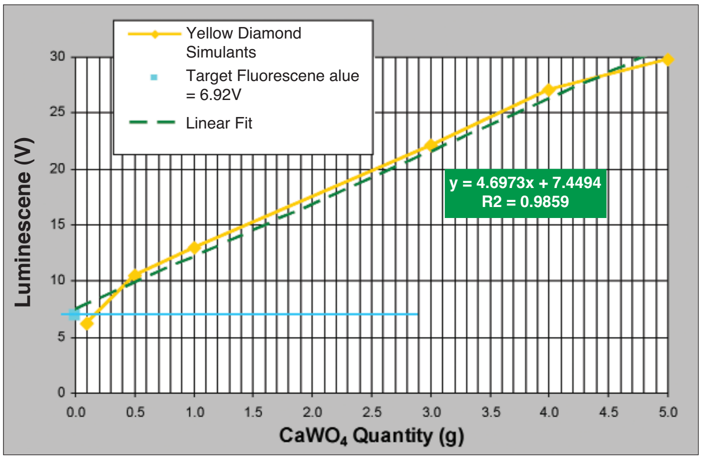

Figure 7—The luminescence responses of the yellow diamond simulants with different quantities of $CaWO_4$

Table IV

The quantities of calcium tungstate added to each recipe

Pigment	Calcium tungstate	Luminescence response
Blue	0.62 g	38.01 V
Clear	0.55 g	21.96 V
Green	0.36 g	9.93 V
Red	0.21 g	8.32 V
Black	0.21 g	7.52 V
Yellow	0.20 g	6.92 V

Figure 8—Samples of the 8 mm cubic diamond simulants

Test with the diamond simulants

A manufacturer of X-ray machines conducted a test with the diamond simulants. The recovery efficiency for each colour coded simulant is documented in Table V.

The partition curve for this data is given in Figure 9, which shows that the 50% detector threshold voltage is 2.25 V, marked 'X'. With this information the manufacturer can quantify the effects of:

- Upgrading the detector technology
- Increasing or decreasing the voltage on the X-ray tube
- Increasing or decreasing the current on the X-ray tube
- General wear and tear on the machine over time.

Discussion

Equipment

This research project depended on the capability and functionality of the optics box, which had to be able to measure the luminescence response of the simulants when processed through different X-ray machines. An X-ray machine is designed to measure either reflected or transmitted luminescence, and the two positions of the PMT provided the necessary versatility. The two PMT positions also facilitated an understanding of omni-directionality of the luminescence in general. The optics box provided an understanding of how the different components of the recipe responded to X ray irradiation.

The dimensions of the optics were such that any simulant or test material placed on the adjustable stand was completely irradiated with X-rays. Extreme care had to be taken when positioning the diamond simulants on the stand in the optics box. If the simulants did not occupy the same spot or were positioned in a different orientation, variations in the measured luminescence occurred. From a geometric calculation, a simulant positioned with a corner pointed to

Table V

An X-ray machine's efficiency in the recovery of diamond simulants

Simulant colour	Luminescence response (V)	Recovery efficiency (%)
Blue	33.01	100
Clear	16.96	100
Green	4.93	100
Red	3.32	95
Yellow	2.52	70
Black	1.92	10

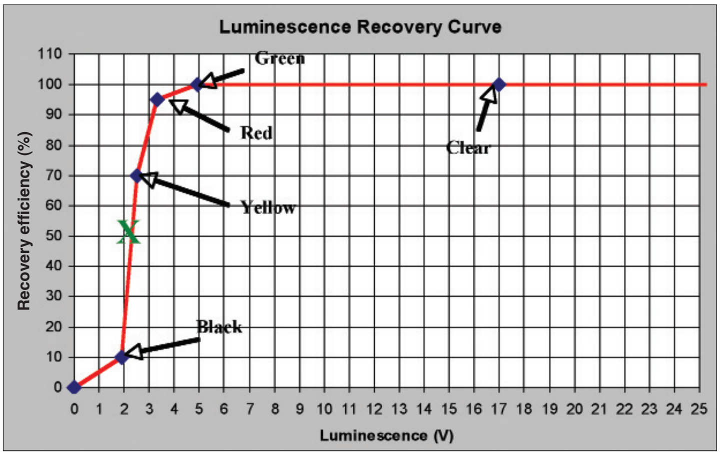

Figure 9—Luminescent recovery curve of an X-ray machine

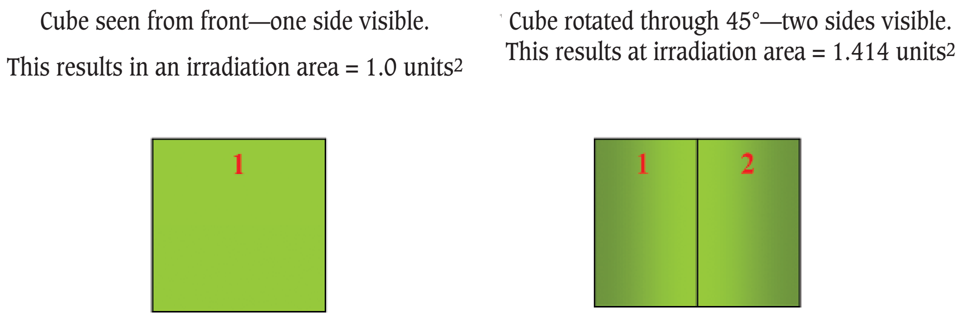

Figure 10—Diagram showing the change in surface area due to different orientations of the diamond simulants

the X-ray tube and thus exhibiting two faces obliquely for irradiation, will receive an additional 41.4% irradiation than a simulant positioned with the flat face pointing to the X-rays, as seen in Figure 10. This geometric variation contributed to the high standard deviations obtained in the measurements on the diamond simulants. Concentric circles were drawn on the stand to improve the positioning of the simulants on the stand and to improve the repeatability of results.

X-ray diamond simulant recipe

Finding the correct combination of ingredients for making up the diamond simulants was more difficult than originally anticipated. However, the final combination and quantities of ingredients used to make the diamond simulants was satisfactory.

Polyurethane is an ideal substance as a bonding agent since X-rays are able to pass through it with no measurable attenuation. The X-rays are able to irradiate and excite the calcium tungstate powder mixed into the polyurethane, enabling the calcium tungstate to luminesce. The luminescence signal emitted by the calcium tungstate is not attenuated by the polyurethane and is detected by the PMT.

The browning of the polyurethane due to long exposures to X-rays is of a minor consequence since the diamond simulants will be exposed to X-rays only for an average of 20 ms each time they pass through an X-ray machine.

The calculations of the amount of lead required as a solid insert (not powder form) in the diamond simulants indicated that there was sufficient volume left in the simulant, where the X-rays could irradiate and excite the calcium tungstate. Although lead highly attenuates X-ray irradiation, it does not interfere with the light paths around it. Secondly, when the calcium tungstate is luminescing, the lead does not appear to interfere with this visible light and therefore the optical luminescence signal is detected by the PMT.

The calcium tungstate powder varied in size from 50 μm to 350 μm and variations in luminescence are expected to decrease as the size range of the powder particles decreases. Tests to determine these effects are to be carried out in the future.

In order to obtain the correct luminescense response from the diamond simulants, a combination of pigment and calcium tungstate was required.

The pigments were transparent to X-rays but the blue and green pigments were found to luminesce when irradiated with X-rays. This was noticed when comparing the luminescence response to that of the clear simulants where no pigment was added (Table II). It is evident from Table II that the red, yellow and black pigments absorb luminescence at 450 nm.

The test carried out on the X-ray machine, as seen in Figure 9, indicates that the diamond simulants can be used to successfully monitor its performance. On the mines a similar test with the diamond simulants would be conducted. The results of such a test would then be compared to the yields obtained from the X-ray machine. If the yields are too high (and the hand sorters are not able to cope with the quantities) then the mine could decrease the sensitivity of the X-ray machine by increasing the 50% detector threshold voltage by a quantifiable amount. If the yields from the X-ray machine suddenly drop, then one would first conduct a test with the diamond simulants to determine if the 50% detector threshold voltage has changed. If there were no changes, then one can conclude that the X-ray machine is operating as required and that the changes in the yield were due to geological reasons—the ore contained fewer luminescent particles.

Conclusions

Colour coded X-ray translucent diamond simulants of different sizes, that luminesced at a wavelength of 450 nm when irradiated with X-rays were successfully produced. These simulants were successfully used to evaluate an X-ray machine.

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