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PNNL-20269

Reducing ^{68}Ge Background in Dark Matter Experiments

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March 2011

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Executive Summary

Experimental searches for dark matter include experiments with sub-0.5 keV-energy threshold high purity germanium detectors. Experimental efforts, in partnership with the CoGeNT Collaboration operating at the Soudan Underground Laboratory, are focusing on energy threshold reduction via noise abatement, reduction of backgrounds from cosmic ray generated isotopes, and ubiquitous environmental radioactive sources. The most significant cosmic ray produced radionuclide is ^{68}Ge. This paper evaluates reducing this background by freshly mining and processing germanium ore. The most probable outcome is a reduction of the background by a factor of two, and at most a factor of four. A very cost effective alternative is to obtain processed Ge as soon as possible and store it underground for 18 months.

Acronyms and Abbreviations

CoGeNT	Coherent Germanium Neutrino Technology
HPGe	High purity germanium detector
PNNL	Pacific Northwest National Laboratory
WIMP	weakly interacting massive particle

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1 Introduction

Experimental searches for weakly interacting massive particle (WIMP) dark matter include experiments with sub-0.5 keV-energy threshold high purity germanium (HPGe) detectors. The science reach will include detector sensitivity to light-mass (<10 GeV/c^2) WIMPs. Experimental efforts, in partnership with the CoGeNT (Coherent Germanium Neutrino Technology) Collaboration operating at the Soudan Underground Laboratory, are focusing on energy threshold reduction via noise abatement, reduction of backgrounds from cosmic ray generated isotopes and ubiquitous environmentally present radioactive sources.

The dark matter signal is a low-energy nuclear recoil producing the equivalent of ~1 keV of gamma-ray-deposited energy in a germanium detector. This energy range is well below many x-rays. Due to the nature of the WIMP-nucleus interactions, progressively more events occur with lower energy nuclear recoils. Thus, the prime objective is to provide the technology to enable detector energy thresholds below the ~0.5 keV currently seen. Based on x-ray detector design, an energy threshold as low as 0.1 keV may be possible.

One of the backgrounds that can be reduced is due to the presence of cosmic-ray-induced radionuclides in the HPGe detector. The most significant of these is from the decay ^{68}Ge with a 271-day half-life. Sensitivity goes roughly as the square root of the background rate, that is, the signal to noise is inversely proportional to the square root of the background, and reducing the background enhances the signal to noise. This background can be reduced by: 1) waiting for the activity to decay, 2) using germanium enriched in ^{76}Ge that has a much lower production rate for ^{68}Ge, 3) mining fresh germanium and processing it rapidly to avoid production of ^{68}Ge, or 4) using germanium that has been stored underground for a few years.

To get a factor of two improvement in signal to noise, one would have to wait for roughly two half-lives of decay, or 1.5 years. An order of magnitude improvement in sensitivity would take 7.5 years of decay time. The cost of ^{76}Ge is about 60 times that of natural germanium. Mining fresh ore is an option if it can be processed within a short time period at a reasonable cost. A stockpile of germanium would need to be created now in order to give sufficient time for decay of the current activity.

2 Background Sources

A method to produce germanium detectors having reduced cosmic ray generated radionuclides is perhaps the single most important technical effort needed to take the CoGeNT detector technology into the future. Why is this so important? Figure 1 shows the results from the most recent CoGeNT paper [1]. Every peak in the spectrum is the result of a cosmic ray initiated process (e.g., neutron capture activation or nuclear spallation). The labels in the figure on the peaks show the parent radionuclide and the atomic x-ray energy of the associated daughter nuclide. These spectral peaks are a background to the dark matter analysis that must extract a limit on an exponential component below 2 keV. Thus, dramatically reducing the 10.4 keV and 1.3-keV peaks (from the decay of ^{71}Ge with a 11.4-day half-life and ^{68}Ge with a 271-day half-life) immediately makes the detector more sensitive, allowing either better limits on dark matter parameters or a better measurement of the potential signal hinted at by the CoGeNT paper [1]. The typical zone refining process, which removes impurities from the germanium crystal, will not remove the ^{68}Ge from the crystal. Thus, germanium that has only had the most minimal surface exposure to cosmic rays is ideal for fabricating future, improved sensitivity CoGeNT-style HPGe detectors.

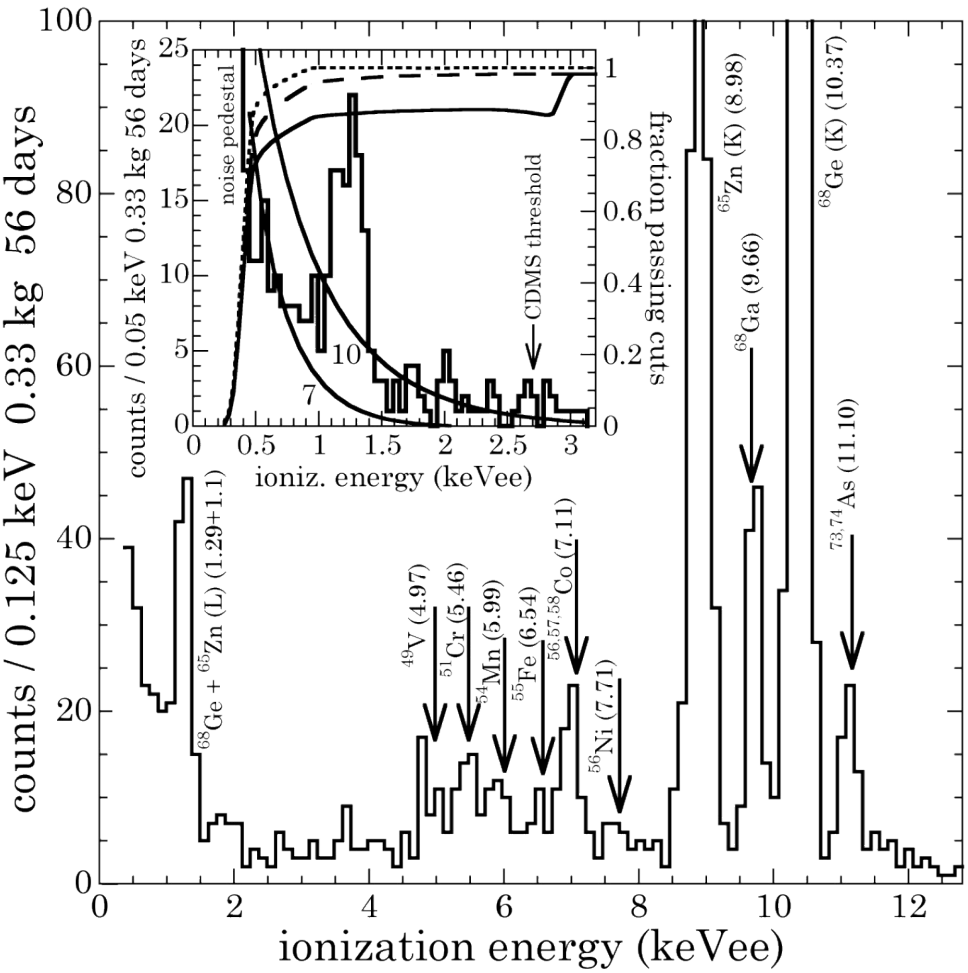

Figure 1. Low energy spectrum from the CoGeNT Collaboration's paper on dark matter limits.

Table 1 shows some details about the K x-rays seen in Figure 1. For example, the cosmic-ray produced ^{68}Ge decays to ^{68}Ga with a 271-day half-life, and the Ga K (10.38 keV) and L x-rays are observed in the detector. The ^{68}Ga then decays to ^{68}Zn (which is stable) with a 67.7-min half-life, and the Zn K (9.67 keV) and L x-rays will be observed. Similarly, the other x-rays observed in Figure 1 result from cosmic-ray produced radionuclide decays, and the decays of their daughters.

Table 1. K-decays observed in CoGeNT data

Parent Radionuclide	Daughter Nuclide	Daughter K-edge Energy (keV)	Parent Half-life
^{73}As, ^{74}As	Ge	11.11	80.3-day, 77.8-day
^{71}Ge, ^{68}Ge	Ga	10.38	11.4-day, 271-day
^{68}Ga	Zn	9.67	67.7-min
^{65}Zn	Cu	8.99	243.7-day
^{56}Ni	Co	7.72	6.1-day
^{56}Co, ^{57}Co, ^{58}Co	Fe	7.13	77.2-day, 271.7-day, 70.9-day
^{55}Fe	Mn	6.55	2.74-year
^{54}Mn	Cr	6.00	312-day
^{51}Cr	V	5.48	27.7-day
^{49}V	Ti	4.98	330-day

3 Production and Decay of ^{68}Ge

Natural Ge is 21.23% ^{70}Ge, 27.66% ^{72}Ge, 7.73% ^{73}Ge, 35.94% ^{74}Ge, and 7.44% ^{76}Ge. Atoms of ^{68}Ge are produced at a rate of about 53.3(43) atoms/(kg-d) in natural Ge [2].[1] It should be noted that the production rate for Ge enriched to 86% ^{76}Ge would have a ^{68}Ge production rate of about 0.5-0.9 atoms/(kg-d) [3].

Atoms are produced as long as the material is above ground. Figure 2 shows an example of a sample of natural Ge exposed above ground for 100 days, 200 days, 400 days and 1000 days, which is then placed underground where the ^{68}Ge decays away. The "400 Day Production" line is production with no decay. The decays of ^{71}Ge are not included in this plot. It can be assumed that ^{71}Ge, with an 11.4-day half-life, will only contribute to the background in the first approximately 100 days after the detector is placed underground, after which the ^{71}Ge will be significantly decayed (down by a factor of over 500).

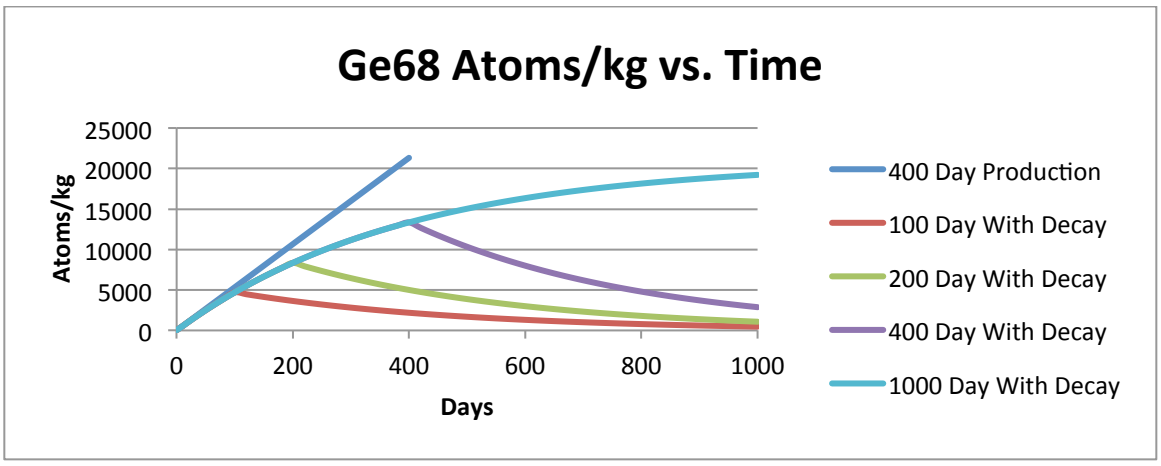

Figure 2. Production and decay of ^{68}Ge assuming a 100-day production period.

With 100 days of exposure, the material has about 4700 atoms/kg. With longer exposures, this asymptotically approaches 20,823 atoms/kg (a factor of 4.4 more atoms/kg than 100 days). This suggests that the exposure time needs to be much less than one half-life of 271 days in order to have any significant positive impact on the experiment by limiting the ^{68}Ge present in the sample, and that an exposure time of less than 100 days is desired. It is probably unrealistic to expect an exposure time of less than 50 days.

If the detector was manufactured with 100 days of exposure, and then placed underground and used to obtain data 100 days later, there would be about 3641 atoms/kg left, which corresponds to a decay rate of about 9.3 decays/day/kg. After 200 days, this is down to about 2818 atoms/kg and a decay rate of 7.2 decays/day/kg. This can be compared to material that is saturated in ^{68}Ge, which would have a decay rate 4.4 times greater. Thus, using Ge that is only exposed for 100 days rather than saturated, and then is underground 100 days before counting, would reduce the background counts in the next 60 days from about 2350 counts/kg to about 530 counts/kg, or about 9 counts/kg/day averaged over this period.

[1] Note that this rate is greater than the 30(7) atoms/(kg-d) determined by Avignone et al. [3].

Each ^{68}Ge decay will produce a Ga x-ray, followed by the beta from ^{68}Ga decay (68-minute half-life). Each ^{71}Ge decay will produce a Ga x-ray; ^{71}Ga is stable. Of these decays, 86.3% are K shell, 11.5% are L shell, and 1.9% are M shell. So for the scenario above, where 530 counts/kg were produced in 60 days, about 61 counts/kg would be at 1.3 keV or about 1 count/kg/day (compared to 270 counts/kg for saturated material, or about 4.5 count/kg/day average). Figure 3 shows the decay rate through the L shell as a function of time for material placed underground after 100 days of exposure. Rejection of counts using the 68-minutes half-life of ^{68}Ga may be practical if limited to one half-life of dead time introduced.

From the CoGeNT article [1] and information from the collaboration, there are about 945 counts in the 10.3 keV peak for a two-month period (uncertain what the cool down period was, but approximately 100 days). This implies there should be about 126 counts in the 1.3 keV line, or about 2 counts/day on average. The HPGe detector used has a mass of 0.33 kg, giving 382 counts/kg in the 1.3 keV line (2863 counts/kg in the 10.4 keV line), or about 6 counts/kg/day average. A more precise calculation using the original data should be performed with the actual cool down period, since this value falls above the value of 4.5 counts/kg/day computed above for saturated material and indicates that the detector had cooled down for less than 100 days.[2]

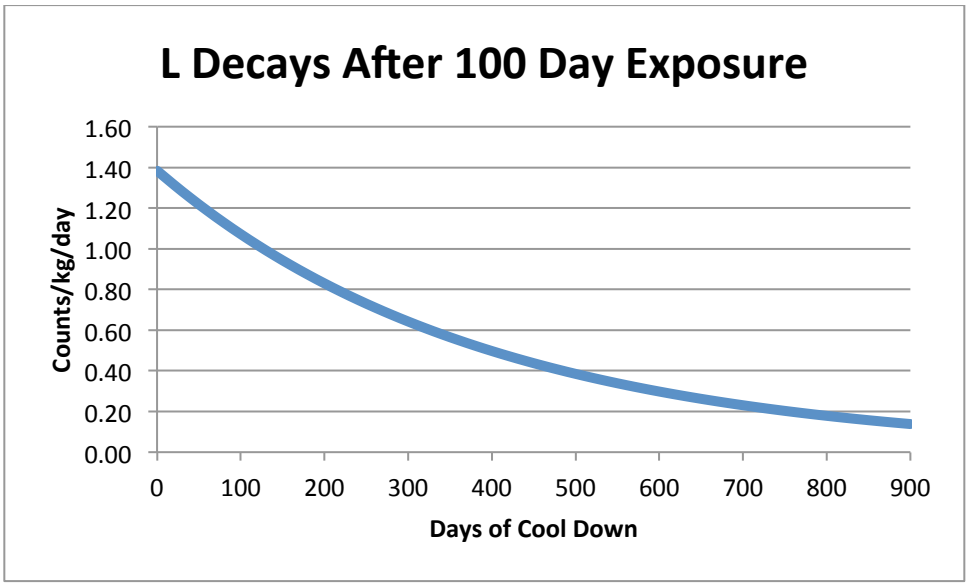

Figure 3. L decay rate for ^{68}Ge underground after 100 days of exposure.

[2] This detector has a complex history since it was used in an experiment near a nuclear reactor, and thus may have some resulting activation. This is indicated by a statement from Juan Collar. This detector went underground at Soudan on August 24, 2009, and data was taken starting December 4, 2009, ~104 days later. Prior to this, the same detector (BEGe-I), which came from Canberra, was installed at SONGS (30 m.w.e.) on November 12, 2008. It came out from SONGS tendon gallery sometime between June 30, 2009 and August 7, 2009. It is reported that thre were ~3766 events in the 10.4 keV peak for 12 months of data, but there is uncertainty about when that counting began. This number would result in an even higher decay rate value.

4 Detector Construction Process

Germanium material delivered for processing into detectors typically arrives as GeO_2. This material may require conversion to a chloride and distillation in order to eliminate chemical impurities; the chloride would then be converted back to oxide. These operations are performed by companies like Umicore before arriving at detector vendors. The oxide material is dried and then reduced to metal in a hydrogen atmosphere, and then zone refined to electrical grade in batches of ~4 kg. This material is then passed to a detector manufacturer where it is zone refined one or more additional times to reach detector grade material. The crystal pulling vendor starts from ~20 kg of melt to grow a crystal. This crystal, if it is of sufficient quality, may produce 1-3 detectors. Normally, the remaining material is then recycled through the zone refine and crystal pulling process. Using this normal recycling, as many as six passes through the process may be required to produce the maximum number of detectors from a starting mass, with about 10 kg of material left behind, and a number of kilograms of lost material. It thus takes about 30 kg of Ge going into the process to produce a batch of ~10-20 kg of detectors, assuming recycling.

But, with only a single pass and no recycling in order to minimize cosmic exposure, 30 kg of Ge might give ~4-6 kg of detectors. This assumes an average 2 detectors per crystal pull, with a minimum of 10 kg/pull, and a desire for 1 kg detectors. It is thus recommended that **30 kg of Ge** should be the base amount of starting material that will be required to guarantee enough detectors can be made for CoGeNT-4. Once the crystal is sliced into blanks, it is processed into functioning detectors. The entire process from clean material to functional detectors can take about 35 days for one pass.

5 Germanium Sources

Germanium is mined primarily from sphalerite [(Zn,Fe)S], the chief ore for zinc, though it is also recovered from silver, lead and copper ores. The 2009 price for Ge was $950/kg, and varied from $600-$1400 over the last decade. Worldwide production in 2006 was roughly 100 tonne of germanium. Currently, it is recovered as a by-product from sphalerite zinc ores where it is concentrated in amounts of up to 0.3%, especially from sediment-hosted, massive Zn–Pb–Cu(–Ba) deposits and carbonate-hosted Zn–Pb deposits. Figures for worldwide Ge reserves are not available, but in the US it is estimated to be around 500 tonne. In 2007 35% of the demand was met by recycled germanium. Another source of germanium is fly ash of coal power plants that use coal from certain coal deposits with a large concentration of germanium. Russia and China used this as a source for germanium. [4]

According to Moskalyk: “The worldwide market for electronic components is very diversified and highly competitive amongst the many nations vying for improved market share. Similarly, germanium must compete with gallium, indium, and rare earth metals in a very selective industry. Niobium and tantalum are sometimes substituted for these metals. The predominant minerals hosting germanium include argyrodite, germanite, and renierite while lead/zinc deposits plus certain coals represent another major source of supply. Germanium is extracted by means of complex processes from zinc residues in particular, which also contain metal values such as cadmium, gallium, and indium. On a global basis, over 20 producers are dedicated to the commercial production of germanium metal and other compounds. The largest consumers of germanium-bearing material are Japan and the USA. Countries such as the United States, Taiwan, Belgium, China, Russia, Germany and Canada are the main producers of germanium while others contribute smaller quantities for worldwide consumption. The supply and demand of germanium products fluctuated during the past two decades and was subjected to a gradual erosion of delivered price for two forms, pure metal and germanium dioxide.” [5]

6 Germanium Supplier Contacts

Suppliers of Ge, such as American Elements (www.americanelements.com) and Alfa Aesar (www.alfa.com) do not control their source. Mines, such as War Eagle Mining mines Ge in Tres Marias, Chihuahua, Mexico (www.wareaglemining.com/s/TresMarias.asp), do not usually deal with end users.

A USGS contact, Dave Guperman (703-648-4977) provided some contacts at mines where Ge is extracted (Tech Resources Limited, Vancouver, Canada, Red Dog Mine. 604-699-4000; and Ge Corp. of Am. Utica, NY, 315-732-3744).

Umicore, formerly Eagle Pitcher, in Quapaw, OK, buys material from mines and turn it into high purity metal. Jim Meyers (417-781-0671), retired from Eagle Pitcher, referred me to Dennis Thomas (918-673-1650) at Umicore for information. Dennis suggested that they could get material from Cominco in British Columbia, either from a mine in Alaska or in Washington, and then refine it to metal. He said other sources, except China, tend to be shallow coal mines or surface mining. Greg Belland is a Cominco Production Manager (Trail, BC, 250-364-4121). The initial thought was to see if Cominco could pull any zinc ore from their Washington mines and immediately concentrate and send to the smelter in Trail for immediate processing on a campaign basis. They also might be able to do this from their mine in Alaska. Maybe they would have a smaller pilot plant where the zinc cons can be run without any cross contamination from material which has been above ground for an extended period. It was learned from Cominco that this scenario would probably not be possible because of the long holdup of the ore above ground.

Commercial Services manager at Cominco (Toronto) Bill Van Beek (250-364-4121) said that their Pend Oreille mine in WA was shut down two years ago. Their Red Dog open pit mine in Alaska accumulates ore on the surface and ships it every 18 months for processing. The ore is 80 ppm Ge, which gets mixed with older remainders material at the 50% level, before going through a refining process. Thus, this location is not timely for a source of fresh Ge.

Bill Van Beek referred us to Kent Strader (931-221-3221; kent.strader@nyrstar.com) at the Gordonsville Nyrstar mine in Clarksville, TN where ore at up to 350 ppm is extracted from an underground mine. According to Robby Westerman at Nyrstar, the ore is mined east of Nashville, and after 500 tons of ore are accumulated (in about 3 days) it is sent the 100 miles to be processed. It is roasted and the Ge is leached out of the ore. The Ge is then shipped to another company (MCP) for final purification. It appears that we may be able to obtain the material from Nyrstar, with an above ground exposure time of ~60 days. The following is information provided by Kent Strader:

> "Nyrstar owns and operates the Middle Tennessee Mines (MTM) in Gordonsville Tennessee. This mining complex was originally started in the early 1970's and expanded over the year to include several mining areas, all within a few miles of the Mill/Concentrator at Gordonsville. The zinc ore is mined at depths of 800' to 1200' and ranges in Ge content from 330 ppm to 475 ppm depending on the specific mining area. At full production, MTM is expected to produce about 100,000 dry metric tons of zinc ore concentrate at 62.6% Zn, 31% S and 350 to 425 ppm Ge, (along with approx. 380 to 445 ppm Ga). The entirety of MTM's production is intended to be consumed at Nyrstar's Clarksville Tennessee zinc smelter.
>
> At Clarksville, the zinc ore concentrate is roasted to drive off the sulfur/sulfide leaving a zinc oxide that is then leached with sulfuric acid. As part of the leaching process, a residue is produced that has the bulk of the impurities and gangue from the concentrate. Ge and Ga report to the residue.

The residue can be filter pressed into a cake for shipment to Ge/Ga recovery plants. As you would expect, most of the metals in residue are oxides and sulfates. The actual Ge content in the residue is a direct function of the Ge units put into roasting. Currently, commercially viable residues need to be greater than 0.20% Ge (Table 2). My expectation is that the maximum concentration of Ge in residue (at 83% MTM, 17% other feed to roasting) would be about 0.55%. For your reference, I have attached the MSDS for the residue, named Germanium Concentrate.

One of the challenges of producing and capturing commercially interesting grades/quantities of Ge residue is having sufficient quantities of MTM zinc ore concentrate. This is currently our biggest challenge as the MTM mine is still in ramp up phase after having been closed for some time. In order to run a successful campaign of MTM concentrates and thus capture the maximum Ge output we must accumulate a minimum of three weeks of roaster consumption, approximately 10,000 metric tons (longer campaigns produce better Ge recovery). At full production rates at MTM, my estimate would be 8 weeks (max) between extraction of the raw ore from underground until production of the Ge residue. Unfortunately, my current expectation is that the first opportunity to run a MTM campaign will be July 2011."

Table 2. Germanium Concentrate Composition

Element	% Weight
Zinc	20.0
Lead	12.0
Iron	20.0
Silica	10.0
Sulfur	12.0
Calcium Sulfate	25.0
Cadmium	0.4
Germanium	0.25

The Germanium Concentrate produced by Nyrstar is thus only 0.25% Ge and requires further chemical processing. To obtain the required 30 kg of Ge, about 12 tonne of this concentrate are required. We will have to work with the company that Nyrstar uses to purify the Ge from this concentrate.

It would take less than a week to accumulate the 12 tonne of Ge concentrate needed to obtain 30 kg of Ge. The critical path would be:

1) Stockpiling of feed from Gordonsville prior to the campaign (perhaps a month after actual mining).
2) Processing/campaigning through the smelter (a full campaign is 3 weeks or so).
3) Accumulation of shippable quantity of Ge concentrate (probably daily shipments to the customer for upgrading while the campaign is on).
4) Processing through the customer to either a higher grade Ge material or all the way to Ge metal (time for this is unknown as we will not be marketing the first campaign material until it is produced, samples, and analyzed).

The processing company would likely be MCP (Kris Guns). MCP says that they send the concentrate to Belgium for processing and could not guarantee any delivery time schedule. Umicore also ships the concentrate to Belgium to their subsidiary. Obviously shipping 12 tonne of material to Europe and getting back 30 kg would take many weeks. I again spoke to Denis Thomas at Umicore, and he said he would check on three options: how fast they could send it to Belgium and get it back, whether they could get Russian mined material and have it processed in Belgium, and whether they could process this quantity in Quapaw, OK. It appears that the concept of deep mining and rapid processing will be difficult.

7 Process and Cost Estimate

The desired process for obtaining the Ge would be for a batch of Zn ore to come out of the mine, be shipped for processing within a few days, processed immediately, and the Ge extracted. From the information gathered, it appears that a baseline of about 100 days of above ground exposure would be possible for obtaining the Ge if it did not have to go to Europe. An underground storage facility would be required to store all Ge when it is not being processed. The Ge coming from the mine and the Ge concentration process would probably require chemical cleaning, and would then be zone refined. The Ge metal would be passed to the detector manufacturing process, which could take an additional ~35 days for crystal pull and detector manufacturing. The material would be placed into the underground storage during this processing whenever possible. Table 3 shows a possible time line for the process. We would have to work to reduce these times in order to get below 100 days.

Table 3. Possible process schedule

Process	Process Time (d)	Total Elapsed Time (d)
Mining and extraction of Ge from ore	60	60
Chemical purification of concentrate (if not sent to Europe)	20	80
Chemical cleaning and first zone refine	5	85
Zone refine and crystal pull	14	109
Detector manufacturing	21	**130**

If the material had to be sent to Europe and returned (via boat), an additional 60 days of process time would likely result.

The cost would include obtaining the raw material, underground storage, chemical cleaning and first zone refining, and then detector manufacturing with this sequestered material, including the cost of having the material moved in and out of underground storage. The current cost of Ge metal is $1.40/g, so 30 kg would cost $42k on the open market. Nyrstar provided an estimate of $5k for 15 metric tons of Ge concentrate. Table 4 provides very rough estimates of costs (a guess by the authors).

Table 4. Cost Estimate

Process	Cost Estimate
Mining and extraction of Ge from ore	$5k
Chemical purification of concentrate	$30k
Chemical cleaning and first zone refine	$15k
Additional cost of detector manufacturing	$30k
Underground Storage (1 year)	$10k
Total additional cost	$90k

8 Recommendations

If the freshly mined Ge is to be pursued, we would need to get firmer commitments on times and costs from companies in order to estimate the impact. A most probable outcome is a reduction of the ^{68}Ge background by a factor of two, and at most a factor of four, for an investment of ~$100k. But, the need to process the material in Europe is a show stopper because of the increased time and the unknown risk of delivering the material on a tight schedule.

The analysis of the ^{68}Ge decay rate for the CoGeNT data should be performed eventually with the actual exposure and cool down periods. The result presented here for the expected decay rate is in fair agreement with the experimental value reported (4.5 compared to 6).

A very cost effective alternative to mining fresh material is to obtain 30 kg of Ge as soon as possible and store it underground (at ~50 feet) for 18 months. This would produce the same background reduction impact as a 100-day extraction and processing effort at a much lower cost. Storing old detectors underground is one way to accomplish this. PNNL has started the process of accumulating such old detectors.

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