



**USE OF LIME FOR THE
TREATMENT OF SOILS
CONTAMINATED BY
HYDROCARBONS**

SCOPE:



**IN MEXICO DUE TO PETROCHEMICALS OPERATIONS
SOME AREAS AROUND THE COUNTRY ARE
CONTAMINATED BY HYDROCARBONS.**

**RECENTLY, THE GOVERNMENT'S REGULATIONS WERE
CHANGED AND NOW THE COMPANYS ARE OBLIGED TO
REPAIR THE DAMAGE.**

WHY THE SOILS ARE CONTAMINATED?



- ⌘ **HYDROCARBON SPILLING**
- ⌘ **PROCESSES LEAKAGE**
- ⌘ **TRANSPORT ACCIDENTS (TRUCKS OR PIPES)**
- ⌘ **PROCESSES DESIGNS (OXIDATION LAGOONS)**
- ⌘ **HUMAN CARELESS**

LIME IS USED IN DIFFERENTS WAYS DEPENDING ON THE PROBLEM CHARACTERISTICS:



- ⌘ THE TYPE OF SOIL (GRAVELS, SANDS, SILTS, CLAYS)**
- ⌘ THE PRESENCE OF HEAVY METALS**
- ⌘ THE PRESENCE OF COMPLEX ORGANICS (ITS IMPORTANT TO AVOID UNDESIRABLE REACTION)**
- ⌘ THE ENVIRONMENT CONDITIONS (TEMPERATURE, RAIN, HUMIDITY).**
- ⌘ THE QUANTITY OF CONTAMINATED SOIL AND THE RATIO TOTAL ORGANICS/TOTAL SOIL.**

WE CAN GENERALIZE THE USE OF LIME IN 4 CASES:



- ⌘ HEAVY METALS IMMOBILISATION**
- ⌘ ORGANIC DISPERSION**
- ⌘ pH INCREASE AND OXIDATION**
- ⌘ DRYING AND CONDITIONING MUD AND SLUDGE**

HEAVY METALS IMMOBILISATION




- ⌘ **WHEN WE FIND HEAVY METALS WITH HYDROCARBONS IN THE SOIL, LIME PRODUCTS HAVE BEEN USED TO RAISE THE pH OF SOILS.**
- ⌘ **THIS TREATMENT IMMOBILISES THE METALS AND ENABLES THE LAND TO BE USED FOR GROWING FORAGE CROPS AND GRASSES.**
- ⌘ **IN THIS SITUATION THE LIME IS NORMALLY USED AS A COMPLEMENTARY ELEMENT OF THE GLOBAL SOLUTION.**

DISPERSION:



- ⌘ **THERE IS A PATENTED PROCESS, KNOWN AS THE DCR* PROCESS, DESCRIBES THE USE OF COATED GROUND QUICKLIME TO DISPERSE MINERAL OILS AND SIMILAR SUBSTANCES.**
- ⌘ **THE COATING DELAYS THE HYDRATION OF THE QUICKLIME, WHICH SUBSEQUENTLY CARBONATES. BECAUSE THE ORGANIC MATTER IS FINELY DISPERSED, IT IS CLAIMED TO BE BIODEGRADABLE.**
- ⌘ **THE PROCESS IS REPORTED TO BE SUITABLE FOR THE TREATMENT OF CONTAMINATED SOILS AND SLUDGES.**
- ⌘ *** “PROCESS FOR THE SAFE ELIMINATION OF MINERAL OILS AND SUBSTANCES SIMILAR TO MINERAL OILS” , GERMAN PATENT APPLICATION DE 3632337A1, 24 SEPT. 1986.**

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- ⌘ **THE PROCESS IS UNDERSTOOD TO HAVE BEEN APPLIED SUCCESSFULLY TO MANY SITES IN EUROPE.**
 - ⌘ **THE TREATMENT UNDOUBTEDLY IMPROVES THE CHARACTERISTICS OF THE SOIL AND SLUDGE AND IMMOBILISES THE ORGANIC MATTER TO A DEGREE. HOWEVER, THERE IS CONCERN AS TO WHETHER THE TREATED MATERIAL MEETS THE REQUIREMENTS OF THE APPROPRIATE LEACHING TEST (FOR EXAMPLE SIMULATES THE EFFECT OF ACIDIC RAIN)**
 - ⌘ **IN MEXICO SOME ENTERPRISES ARE USING NOW A TECHNOLOGY CLOSE TO THE DCR, BUT THEY MIX DIRECTLY THE LIME (QUICKLIME) WITH THE SOIL AND ADD AN EMULSIFYING AGENT WITH VERY GOOD RESULTS REPORTED.**

pH INCREASE AND OXIDATION:




- ⌘ WHEN THE SOIL IS CONTAMINATED WITH A MODERATE CONCENTRATION OF HYDROCARBONS (INCLUDING OTHER ORGANICS) THE ORGANICS ARE OXIDISED BY OXIGEN “DISOLVED” IN SATURATE LIMEWATER.**
- ⌘ THE ROLE OF THE LIME IS PRESUMABLY TO MAINTAIN THE ALKALINE CONDITIONS FAVOURING THE HYDROLYSIS OF THE ORGANIC MATTER AND TO REACT WITH INORGANIC OXIDATION PRODUCTS SUCH AS SULFURIC ACID.**
- ⌘ A PATENTED PROCESS*USE THIS TECHNOLOGY BUT IN THE PULP AND PAPER INDUSTRY, IN THAT RESEARCH THE ORGANICS ARE OXIDISED IN 20-40min. AT 90-170BARS AND 220°C.**
- ⌘ IN PRACTICE SOME COMPANYS ARE MIXING DIRECTLY MILK OF LIME WITH THE SOIL AND SUPPLAYING O2 FROM AIR BY A BLOWER, AND MAINTANING 150°C. WITH WATER STEAM WITH GOOD RESULTS.**
- ⌘ * “WET OXIDATION FOR PULP AND PAPER INDUSTRY WASTES” ENVIRONMENTAL SCIENCE & ENGINEERING, JUNE 1996.**

WHAT ABOUT THE POLYCHLORINATED BIPHENYLS (PCB's) ?:

- ⌘ **CONSIDERABLE INTEREST WAS GENERATED IN 1990/91 BY REPORTS ARISING THE US ENVIRONMENTAL PROTECTION AGENCY STATING THAT THE USE OF QUICKLIME TO STABILISE PCB-CONTAMINATED SOIL HAD (APPARENTLY) LED TO THE DISAPPEARANCE OF THE PCB's.**
- ⌘ **HOWEVER, IT SUBSEQUENTLY APPEARED LIKELY THAT THE PCB's HAD NOT BEEN DESTROYED (*1).**
- ⌘ **INDEED, THE SUGGESTION WAS MADE THAT, IF QUICKLIME WERE ABLE TO REPLACE CHLORINE ATOMS IN PCB's BY HYDROXYL GROUPS, THE REACTION PRODUCTS MIGHT BE MORE HAZARDOUS THAN THE PCB's (*2).**

- ⌘ ***1- R.L. EINHAUSEAL., "THE FATE OF POLYCHLORINATED BIPHENYLS (PCB's) IN SOIL FOLLOWING STABILIZATION WITH QUICKLIME", EPA/600/2-91/052, SEPT. 1991.**
- ⌘ ***2- W. GRUBER, "TREATING PCB's WITH QUICKLIME" , EI DIGEST 6, JUNE 1991.**



⌘ **SUBSEQUENT TRIALS WERE REPORTED(*, **), IN WHICH PCB'S WERE MIXED INTIMATELY WITH QUICKLIME USING A BALL MILL AS A REACTOR, WHICH ALSO RESULTED IN THEIR APPARENT DESTRUCTION. IT IS UNDERSTOOD, HOWEVER, THAT THE EXPECTED REACTION PRODUCTS WERE NOT DETECTED IN THE PREDICTED QUANTITIES.**


⌘ *** S. BORMAN, "NOVEL IDEA DEVELOPED TO DESTROY TOXIC CHEMICALS" , C & EN, OCT. 11, 1993.**

⌘ **** "LIME USED IN DESTROYING PCB's", LIME-LITES, VOL LX, JAN.-JUNE 1994 (BASED ON AN ARTICLE IN CHEMICAL ENGINEERING, JUNE 1994).**

PRACTICAL CASE:




- ⌘ IN TABASCO MEXICO, NEAR THE GULF OF MEXICO, SLUDGES FROM DRILLING, PRIMARY AND SECONDARY DISTILLATION WERE MIXED AND SENT IN TO A “OXIDATION LAGOON”.**
- ⌘ THESE SLUDGES CONSIST OF CONCENTRATED UNSTABILIZED ORGANICS (MOST OF THEM HYDROCARBONS) WITH INERT INORGANICS (SAND AND CLAY).**
- ⌘ AFTER SOME TIME, THE SOILS ALL AROUND THE LAGOON AREA WERE CONTAMINATED BY THE SLUDGE.**

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- ⌘ **FIRST: THEY TEST THE LIME TREATMENT IN A LABORATORY (CONTROLLING ALL CONDITIONS).**
 - ⌘ **SECOND: WITH THE RESULTS OF TRIALS THEY OPTIMIZED THE LIME-SOIL RATIO**
 - ⌘ **THEN THE “IN SITU” TREATMENT WAS STARTED.**

THE TREATMENT:



- ⌘ **1- THE LAGOON WAS DEWATERED.**
- ⌘ **2- THE SLUDGES IN THE FLOOR OF THE LAGOON WERE MIXED WITH 8% OF HYDRATED LIME (80% $\text{Ca}(\text{OH})_2$) AND COLLECTED IN MANY STOCKPILES.**
- ⌘ **THE TOTAL TREATED DEEP WAS 120cm (2 STEPS 60cm EACH ONE).**
- ⌘ **3- THE SOIL AROUND THE LAGOON WAS ALSO TREATED WITH 5% HYDRATED LIME (80% $\text{Ca}(\text{OH})_2$) AND 60cm DEEP (1 STEP).**

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- ⌘ **4- FINALLY THE “STOCKPILES” WERE SPREAD AFTER 48 HOURS.**
 - ⌘ **TWO WEEKS LATER THE pH LEVEL WAS 9.3 AND THEN THE SOIL WAS ADDED WITH A SPECIFIC BACTERIA USED TO DIGEST THE RESIDUAL HYDROCARBONS.**
 - ⌘ **5- THEN, THE LAGOON WAS FILLED UP WITH WATER FROM A NEAR RIVER.**
 - ⌘ **AFTER 1 YEAR PEOPLE SAID THAT THE RESULTS ARE “SPECTACULAR”**

CONCLUSIONS:



- ⌘ **IN GENERAL THE PROCESS (SOIL TREATMENT) IS UNDERSTOOD BUT THERE ARE SOME COMPANYS USING IT WITH GOOD RESULTS.**
- ⌘ **IN MEXICO IT IS DIFFICULT TO OBTAIN GOOD DATA ABOUT THE SUBJECT BECAUSE IT'S A "TECH-SECRET".**
- ⌘ **THE POTENTIAL IS VERY HIGH BUT WE HAVE TO LOOK OUT WITH UNDESIRABLE REACTIONS AND WITH ENVIRONMENTAL CONDITIONS.**
- ⌘ **WE HAVE TO WORK CLOSE TO THE PEOPLE THAT ARE USING THE TECHNOLOGY TO BE ABLE TO UNDERSTAND WHAT HAPPEN AT CHEMICAL LEVEL AND WHAT WE CAN IMPROVE IN LIME OR IN KNOW-HOW THAT AID THE RESEARCH AND DEVELOPMENT.**